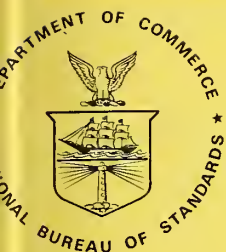


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Standard Reference Materials:

Micro-Homogeneity Studies of NBS Standard Reference Materials, NBS Research Materials, and Other Related Samples

**R.B. Marinenko, K.F.J. Heinrich,
and F.C. Ruegg**

**National Measurement Laboratory
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List of Tables

<u>Table No.</u>	Page
I. Standard Reference Materials and Research Materials which are Tested for Microscopic Homogeneity.	3
II. Specifications for Periodic Integrator Assembly.	12
III. Homogeneity Study of SRM 661	25
IV. Homogeneity Study of SRM 662	26
V. Homogeneity Study of SRM 663	27
VI. Homogeneity Study of SRM 664	28
VII. Comparison of Random Sampling with Homogeneity Traces for Iron and Steel SRMs	30
VIII. Homogeneity Study of Low-Alloy Steel SRMs 461 and 463.	32
XI. Homogeneity Study of Gold-Copper Alloy SRM 482 .	34
X. Homogeneity Testing of Cartridge Brass SRM 478 .	36

List of Figures

<u>Figure No.</u>	
1. Conventional ratemeter trace of molybdenum, chromium, and manganese in the steel SRM 663. .	5
2. Periodic integrator homogeneity traces of manganese, chromium, and molybdenum simultaneously recorded from NBS SRM 663 steel.	7
3. Periodic integrator homogeneity traces of manganese and chromium simultaneously recorded from NBS SRM 663 steel.	8
4. Periodic integrator homogeneity traces of aluminum and barium simultaneously recorded from NBS Glass K-489.	10
5. Periodic integrator including scalars, ratemeter, and recorder.	11

List of Figures (continued)

<u>Figure No.</u>	Page
6. Interfacing of the periodic integrator with the electron microprobe and the recorder.	13
7. Cross-section of SRM 664.	20& 21
8. Cross-section of SRM 663.	22
9. Longitudinal cross-section of SRM 662	23
10. Periodic integrator homogeneity trace of tungsten and molybdenum simultaneously recorded from SRM 480	35
11. Periodic integrator homogeneity trace of zinc and copper simultaneously recorded from NBS SRM 478 Cartridge Brass	38
12. Periodic integrator homogeneity trace of lead and silicon simultaneously recorded form NBS RM Glass K-493	40
13. Periodic integrator homogeneity trace of germanium and lead simultaneously recorded from NBS RM Glass K-491.	42
14. Periodic integrator homogeneity trace of silicon, barium, and zinc simultaneously recorded from NBS RM Glass K-489.	42
15. Periodic integrator homogeneity trace of aluminum, phosphorus, and mangesium simultaneously recorded from NBS RM Glass K-497	43

Table of Contents

	Page
I. Introduction	2
New Homogeneity Testing.	4
General Description	4
Instrumentation	9
Statistical Evaluation of Data.	12
II. Results	15
Iron and Steel SRMs 661, 662, 663, 664	17
Low-alloy Steel SRMs 461 and 463	31
Gold-Silver and Gold-Copper Wires, SRMs 481 and 482	31
Tungsten - 20 Molybdenum Alloy, SRM 480.	33
Cartridge Brass, SRM 478	36
Iron-Three Percent Silicon, SRM 483.	37
Glasses for Microanalysis, RM-30	39
Austenitic Iron-Chromium-Nickel Alloy, SRM 479a.	39
References.	45
Appendices.	46

Abstract

A simple routine technique for studying homogeneity in the micrometer range with the electron microprobe has been developed. For graphic display, a digital periodic integrator is used. In conjunction with scalers and a stepping motor on the sample stage, traces similar to industrial control charts based on a comparison of the experiment with the expected (Poisson) counting statistics are quickly obtained. A computer program has been developed to numerically evaluate sample homogeneity.

Several Standard Reference Materials (SRMs) have been tested. These include the iron and steels (SRMs 661-664, 461, and 463), the gold-copper and gold-silver alloys (SRMs 481 and 482), the tungsten-20 percent molybdenum alloy (SRM 480), cartridge brass (SRM 478), the iron-3 percent silicon alloy (SRM 483), and the new iron-chromium-nickel alloy (SRM 479a). A Research Material, Glasses for Microanalysis (RM-30), has also been tested.

Key Words: Digital periodic integrator; electron microprobe; homogeneity; Standard Reference Materials; steel.

I. Introduction

The development and refinement, since the 1960's, of sophisticated instrumental techniques for determining the elemental composition of microscopically small areas have imposed stringent requirements upon reference materials to be used for this purpose. The analyst often requires that the composition assigned to the bulk material should apply as well on the micrometer (μm) scale. This occurs in the testing of samples by techniques such as spark source mass spectrometry which can sample an area as small as $25\ \mu\text{m}$ in diameter, electron probe microanalysis (EPMA) in which typically a sphere about $1\text{-}3\ \mu\text{m}$ in diameter is analyzed, and secondary ion mass spectrometry (SIMS) which may sample a cylindrical volume as small as $1\ \mu\text{m}$ in diameter and $10\ \text{nm}$ deep. Those NBS Standard Reference Materials (SRMs) and Research Materials (RMs) that have been found useful for microanalytical techniques are listed in Table I.

In earlier homogeneity studies conducted in our laboratory with the EPMA [1,2]¹, existing metal Standard Reference Materials which had been certified in bulk were examined. These materials included low-alloy steels (SRMs 461 and 463) and cartridge brasses (SRMs C1102 and 1102). Ratemeter line scans were used for graphic display of linear traces across the samples, and the extent of homogeneity was defined statistically from many random samplings with a $1\text{-}4\ \mu\text{m}$ electron beam.

Some SRMs were specifically prepared with microhomogeneity in mind. The first of these was SRM 480, a tungsten-20 percent molybdenum alloy [3,4]. Ratemeter line scans were used as a preliminary homogeneity check. A point-by-point analysis was then made with a quantitative raster scanning (QRS) technique which electronically displaced the electron beam. The raster size in these analyses was $48\ \mu\text{m}$ on an edge with ten different points along each, giving a total of 100 points in each raster.

The gold-silver (SRM 481) and the gold-copper (SRM 482) alloys were also carefully prepared to be microscopically homogeneous. For the studies of these SRMs [5] a computer-controlled sampling procedure was developed. Again, the electron beam was electronically moved in a one- or two-dimensional raster with preselected distances between points. The data were automatically recorded on magnetic tape and statistically evaluated by TOPO, a data reduction computer program for homogeneity studies [5].

¹Figures in brackets indicate the literature references at the end of this paper.

Table 1. Standard Reference Materials and Research Materials which are Tested for Microscopic Homogeneity^a

<u>No.</u>	<u>Type</u>	<u>Form</u>	<u>Elements (nominal wt %)</u>
SRM 478	Cartridge Brass	Cube and Cylinder	Cu-73; Zn-27
SRM 479	Fe-Cr-Ni Alloy	Wafer	Fe-71;Cr-18;Ni-11
SRM 480	Tungsten-20% Molybdenum	Wafer	W-78;Mo-22
SRM 481	Gold-Silver	Six Wires	Au-100;80;60;40; 20;0 Ag-0;20;40;60; 80;100
SRM 482	Gold-Copper	Six Wires	Au-100;80;60;40; 20;0 Cu-0;20;40;60; 80;100
SRM 483	Iron-3% Silicon	Platelet	Fe-97;Si-3
RM 30	Glasses for Microanalysis	Slices	10 Compositions of Various Oxides
RM 31	Glass Fibers for Microanalysis	Fibers	10 Compositions of Various Oxides

^aTaken from "NBS Standard Reference Materials for Electron Probe Microanalysis and Scanning Electron Microscopy," 1976, an advertising brochure published by NBS.

There were several disadvantages in using this testing procedure. Firstly, it was dependent on a computer external to the laboratory. If the computer was inoperative or if on-line interruptions occurred, no information was obtained, or the stored information was erratic. Secondly, the program TOPO can handle only two elements simultaneously although as many as four elements could be studied simultaneously. Both of our electron probe instruments have three crystal spectrometers and a lithium-drifted silicon detector for analyses of more complex samples. Thirdly, the defocusing of the crystal spectrometers becomes a problem limiting the maximum length of the electron beam scan in either dimension on the specimen

to 40-50 μm . Fourthly, random sampling is not quite adequate because the dimension of uniform regions within the inhomogeneous sample cannot be estimated and conventional analog ratemeter traces cannot be relied upon to reveal such information.

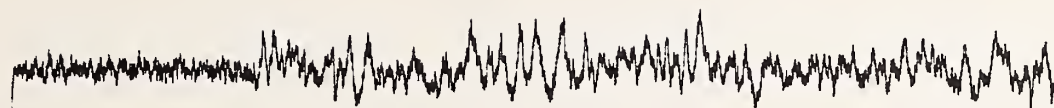
We therefore sought a less complicated and less limiting procedure for studying microhomogeneity. This is described below.

New Homogeneity Testing Procedure

General Description

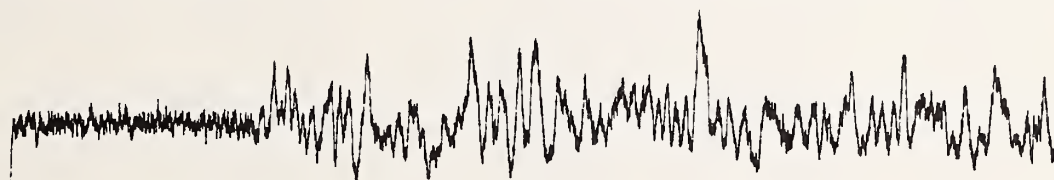
We required a simple procedure which could be performed quickly with our equipment and independently of external systems. A ratemeter scan is a good solution because it can provide a quick visual interpretation of the level of homogeneity. (With TOPO, which relied on two external computer manipulations, no visual data were available until the statistics had been computed.) But the conventional analog ratemeter scan is unsatisfactory because of the difficulty in assigning Poissonian confidence limits to ratemeter excursions and thus in separating real composition changes from statistical fluctuations. This can be seen in figure 1 which is a conventional analog ratemeter trace of molybdenum, chromium, and manganese in SRM 663 which is moving continuously under a 1 μm beam. The average concentrations of these elements are 0.30, 1.31, and 1.50 weight percent respectively. There is a distinct difference between the fluctuations of the signal from the sample when moving and when still, yet limits due only to counting statistics cannot be accurately assigned. The molybdenum concentration is so low here that there is no perceptible signal above the background.

A periodic integrator, such as previously described by Heinrich [6] but based on digital operations (i.e., on a microcomputer), was constructed at NBS. The total number of counts acquired by the scalers in a preselected time period (e.g., 10 s.) is output simultaneously to a teletype (digitally) and to a fast strip chart recorder. The analog signal on the recorder is related linearly to the number of counts in the preceding signal collection period, and remains unchanged until the next time period is completed. A stepping motor on the specimen stage of the electron probe is also controlled by the periodic ratemeter. Between counting periods the stage can be advanced from 1 μm up to 10 μm and the data collection at each spot on the specimen can be repeatedly sampled from 1 to 15 times. In addition, the signal can be digitally multiplied by any appropriate factor and a bias can be applied to digitally subtract any desired count rate



Manganese 1.50 wt. %

Sample
not moving



Chromium 1.31 wt. %

20 μ m beam

1 μ m beam

Molybdenum .030 wt. %



Figure 1. Conventional ratemeter trace of molybdenum, chromium, and manganese in the steel SRM 663. On the right side of the trace, the sample was moving under a 1 μ m electron beam. To the left, the sample was stationary under a 20 μ m beam.

from the signal display. This enhances the excursions of the signal on the chart to any desired level.

An example of the graphic display is shown in figure 2 of SRM 663. The homogeneity trace was prepared with a 1 μm electron beam moving in steps of 1 μm across the sample (visible inclusions were avoided). The operating voltage was chosen so that the effective diameter of the excited area did not exceed 2 μm . Counts were accumulated once on each step for ten-second counting periods. The shaded area through the center of each trace represents a range of $\pm 3\sqrt{N}$ around the average number of counts per period, N . According to Poisson counting statistics, the square root of the mean number of counts collected in a counting period is an unbiased estimate of its standard deviation; $\sqrt{N} \approx \sigma$. Hence, a 99.7 percent confidence limit for Poisson counting statistics applies to the range in the shaded area; deviations outside this region represent specimen inhomogeneity or instrumental variations at the 99.7 percent confidence level. With the traces presented here, it can be easily observed that the graphic representation of step scans provides information on the spatial distribution of elements along the line of scan, and, if several elements are observed, of the degree of correlation between changes in the concentrations of these elements.

The degree of homogeneity required depends upon the intended use of the sample; measurement conditions can be chosen so that the Poisson limits are within the desired level of homogeneity. For example, the beam intensity, operating potential, and time period of signal collection can be adjusted to render these confidence limits congruent with the required accuracy of the measurement. Note that in figure 2 chromium and manganese show large deviations which coincide spatially for these two elements. The molybdenum signal falls within the shaded region because of poor counting statistics. Only the background level is being observed here.

To the left of the figure is a trace recorded from repeatedly counting for ten-second intervals on a stationary 20x20 μm^2 area. The signal from an area this size should be close to the average concentration value for this sample and such repetitions should lie within Poisson counting statistics which they do here. This test verifies that excursions outside the ± 3 -sigma range in the right trace are in truth due to the sample variability and not to instrumental factors such as drift and instability.

Figure 3 shows another ratemeter trace of the chromium and manganese distributions across a specimen of the same standard (SRM 663). Instrumental conditions here were nearly the same as in figure 2 except that an electron beam of 2 μm diameter was used here, and for each 2 μm step across the

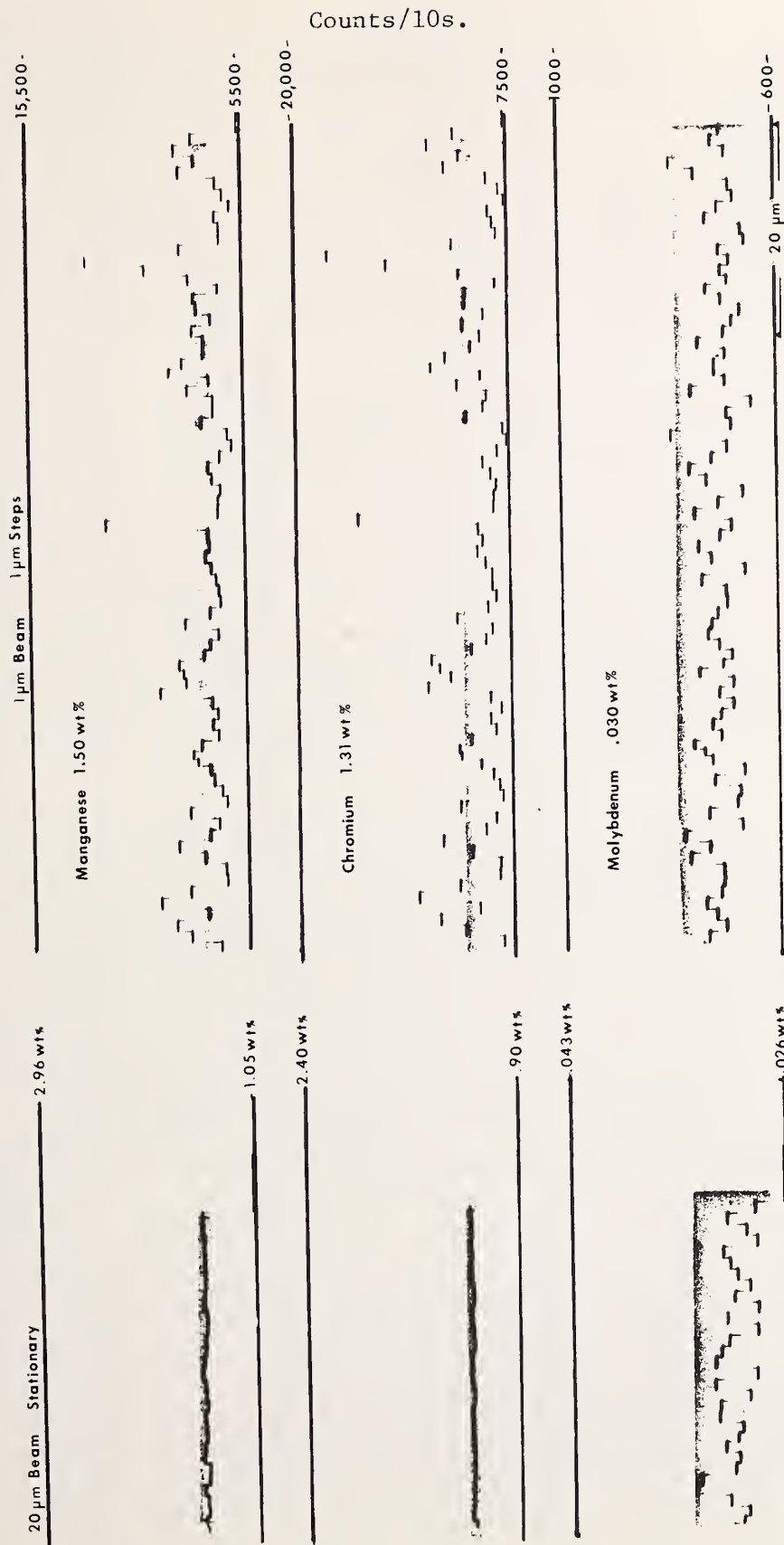


Figure 2. Periodic integrator homogeneity traces of manganese, chromium, and molybdenum simultaneously recorded from NBS SRM 663 steel (voltage = 30 kV, beam current = 1.3×10^{-8} A). In the traces on the right, the sample was advanced 1 μ m electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μ m beam. The shaded regions represent a range of $\pm 3\sqrt{N}$ around the average numbers of counts per 10 seconds, N, for the entire trace.

NBS STEEL SRM 663

2 μ m beam 2 μ m steps

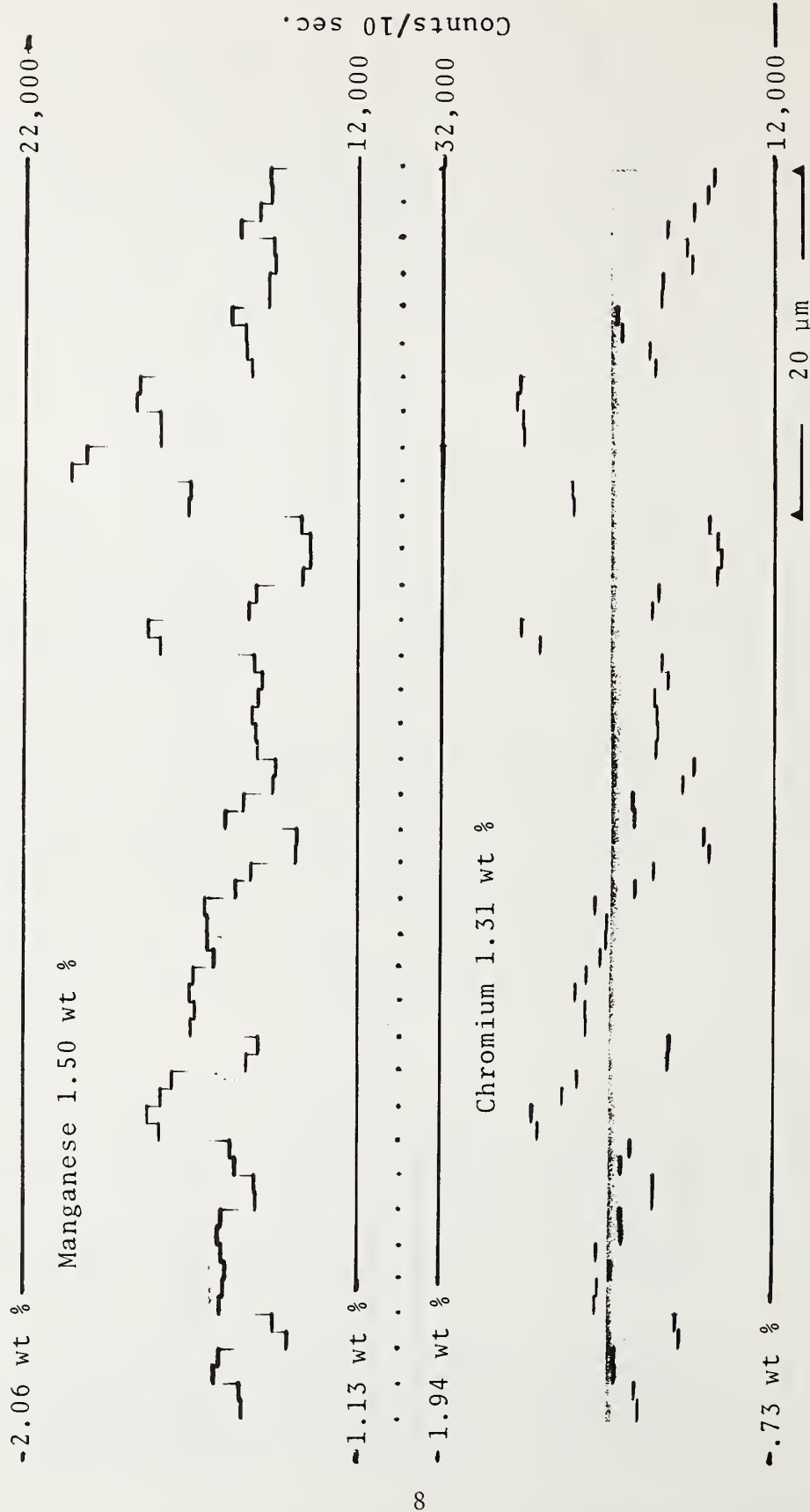


Figure 3. Periodic integrator homogeneity traces of manganese and chromium simultaneously recorded from NBS SRM 663 steel (voltage = 30 kV, beam current = 3×10^{-8} A). The sample was advanced in 2 μ m steps under a 2 μ m beam after two consecutive 10-second counting periods on the same spot. These advances are marked by dots at the center of the trace. The shaded regions represent a range of $\pm 3\sqrt{N}$ around the average number of counts per 10 seconds, \bar{N} , for the entire trace.

sample duplicate 10-s. readings were recorded. Movement of the specimen from one location to the next is indicated in the figure by the dots between the two traces. Differences between steps which are not attributable to counting statistics alone are clearly observable, but repetitive measurements on the same step are in quite good agreement, i.e., within counting statistics. Such a mode of operation permits a statistical comparison of the counting variations within a spot and from spot to spot. This figure again proves that the large variations from one position across the sample to another are indeed due to inhomogeneity.

We have also been using the periodic integrator to characterize glasses prepared specifically for microanalytical work and to test homogeneity in the micrometer dimensional range. Traces for the aluminum $K\alpha$ and barium $L\alpha_1$ signals in NP^c Glass K-489 are shown in figure 4. In both cases - the moving 1 μm beam and the stationary 20 μm beam - deviations are within Poisson counting statistics. These two elements thus are homogeneously distributed in this glass, within the statistical limits indicated on the graph. The above observation of homogeneity can be made in only one stepping direction at a given time. This is a limitation of the procedure. At least one other trace perpendicular to the one above or preferably several more are required to guarantee homogeneity.

One must be careful, though, not to assume that homogeneity is within desirable limits simply because the signal excursions from a traverse across a specimen fall within the Poisson limits for a given set of operating conditions. Where the average number of counts collected per point is low, such as for molybdenum in the SRM steel 663 and aluminum in glass K-489, the ± 3 -sigma limit imposed by Poisson counting statistics alone is quite large relative to the average number of counts per point. Where possible, therefore, the total number of counts in such a case should be increased by adjusting experimental conditions. Also, a statistical comparison between the moving and the stationary specimen is helpful in separating the effect of inhomogeneity from instrumental instability.

Instrumentation

The periodic integrator shown in figure 5 consists of the following components: (1) a single-board microcomputer, (2) a multichannel digital scaler/timer, (3) four digital-to-analog converters with four-digit resolution, and (4) a four-channel fast-pen-response recorder. Specifications for the periodic integrator are listed in Table II.

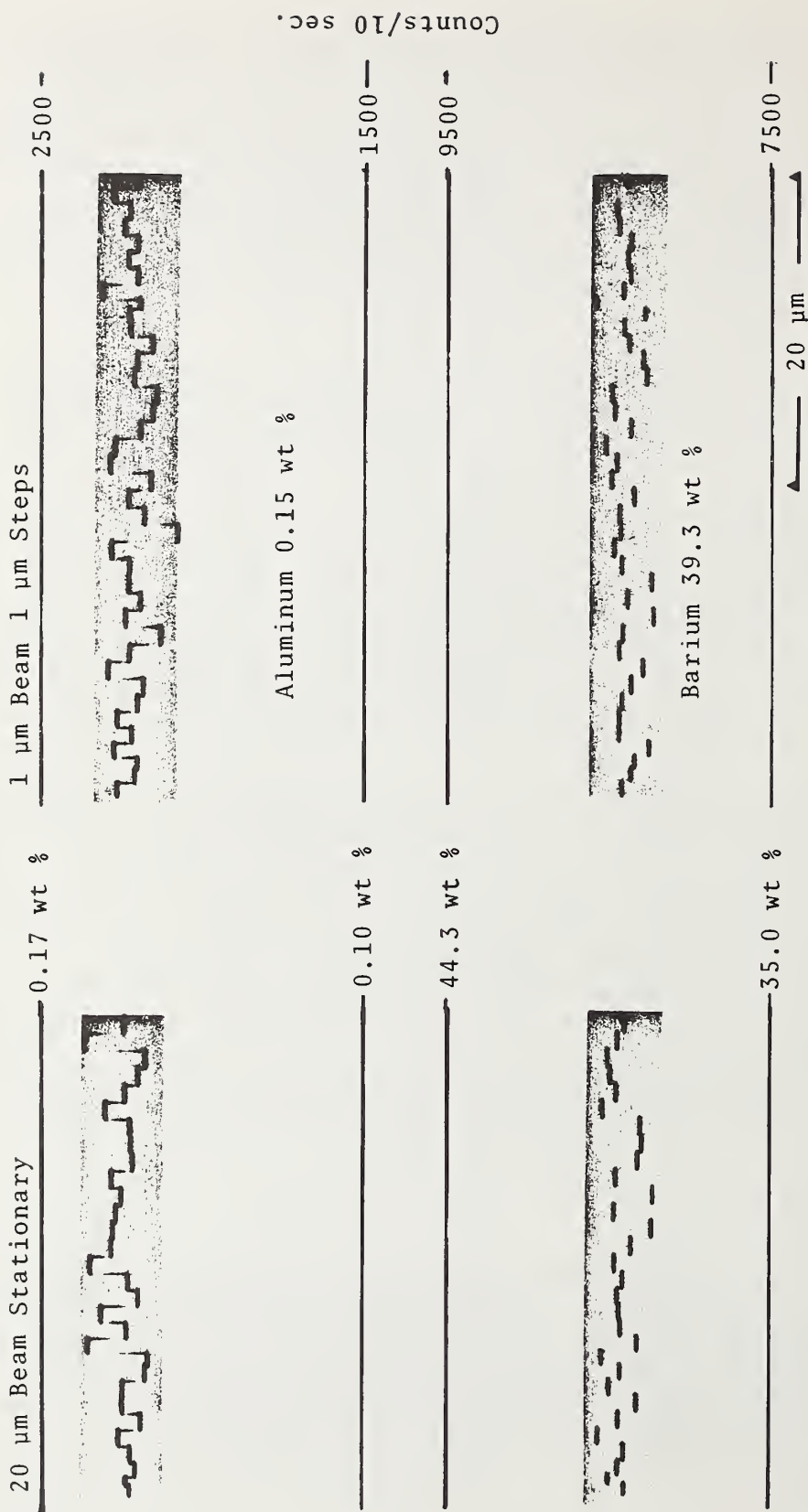


Figure 4. Periodic integrator homogeneity traces of aluminum and barium simultaneously recorded from NBS Glass K-489 (voltage = 15 kV, beam current = 6×10^{-8} A.) In the traces on the right the sample was advanced 1 μ m under a 1 μ m electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μ m beam. The shaded regions represent a range of $\pm 3\sqrt{N}$ around the average number of counts per 10 seconds, \bar{N} , for the entire trace.

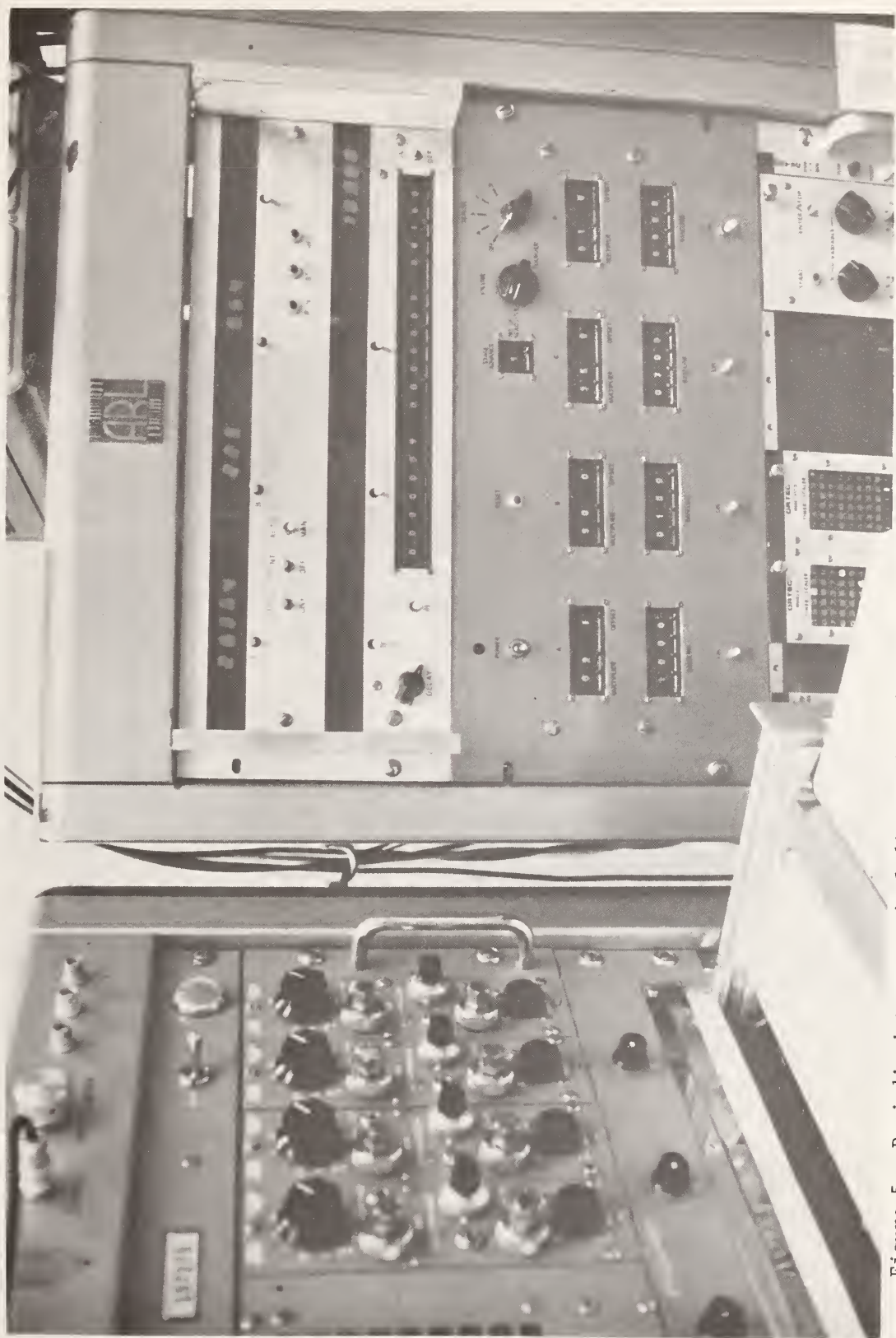


Figure 5. Periodic integrator including scalars (above), ratemeter (below), and recorder (left).

Table II. Specifications for Periodic Integrator Assembly.

Scalers:

Input Level: TTL 0 to +5 volts

Scaler Capacity: 7 digits

Maximum Count Frequency: 10 MHz

Time Base: Crystal controlled, accurate to 1 part in 10^5

Scaler Accuracy: ± 1 count

Data Output: 8 bit parallel ASCII byte serial

Microcomputer Section:

Data Input: 8 bit parallel ASCII byte serial

Calculation Accuracy: Log mode, $\pm 0.3\%$
Linear mode, 4 digits

Data Output: 0 to +5.000 volts

The microcomputer is programmed to receive data from four seven-digit scalers and to operate on any selected group of four adjacent digits out of the field of seven. The following operations are performed by the microcomputer: (1) subtract a four-digit baseline, (2) multiply the result by a two-digit multiplier and (3) compute the \log_{10} of the result if a log display is desired.

The computed results are transferred by the microcomputer to the four digital-to-analog converters, and the analog outputs are connected to a multi-pen strip chart recorder for display. The microcomputer can also advance the stage of the electron microprobe to a new position after one to sixteen scaler read-outs. A block diagram of the interfacing components is shown in figure 6.

Statistical Evaluation of Data

The periodic ratemeter traces described above can be acquired rapidly. If desired, the data can at the same time be recorded numerically on a teletype and stored in an appropriate recording device such as magnetic tape for later statistical analyses.

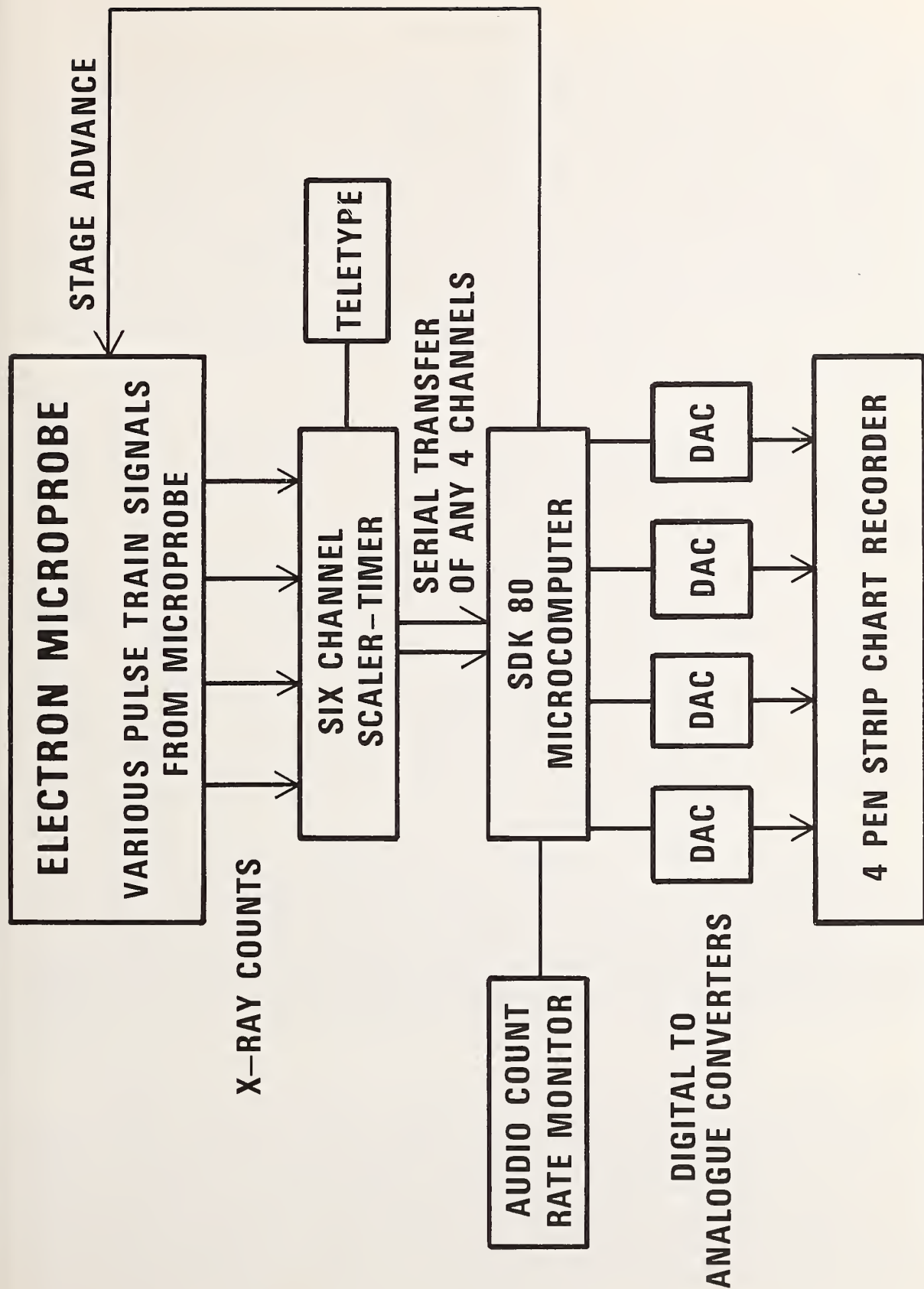


Figure 6. Interfacing of the periodic integrator with the electron microprobe and the recorder.

The computer program we have been using was written by Dr. Robert Paule of the National Measurement Laboratory, NBS. It takes into account three types of signal fluctuations that can occur. These are: (1) those due to concentration differences from point to point, (2) the signal variation on a single point due only to Poisson counting statistics, and (3) the signal drift due to contamination build-up and instrumental instability. To account for the latter two types of signal fluctuations, the Paule program can handle as many as 20 duplicate measurements on a single point (though we are instrumentally limited to 16) for as many as 50 independent points. For each group of duplicate measurements on a single point, an average and a standard deviation are calculated, and also an overall mean and standard deviation are obtained.

By a simple analysis of variance we obtain an estimate of the standard deviation for one point as well as an estimate of the standard deviation between points. These estimates are called the "within" and "between" components of the standard deviation.

The "within" component reflects the variation found in duplicate measurements caused by fluctuations in counting and from instrument drift if present. The "between" component reflects only the variation observed from point to point, excluding the previously mentioned sources of fluctuations. If the "within" and "between" components are quite different, i.e., if the latter is several times larger than the former, a high degree of inhomogeneity of the element or elements in the sample is assumed. The equations used for these calculations are in Appendix 10.

A second computer program is sometimes used. This is an OMNITAB statistics program which was developed at NBS for general usage [7]. We use it to plot the average of the counts for each point, calculated in the previous program, vs. sequence. In addition, OMNITAB calculates many statistical parameters such as the mean, range, standard deviation, variance, etc. of the total number of counts.

II. Results

The homogeneity test procedure described above was used to study several SRMs. These include the iron and steel SRMs 661, 662, 663, 664, 461, and 463, which had not been certified for microanalysis. Some SRMs that had been certified for microanalysis, such as the gold-silver alloys (SRM 481), the gold-copper alloys (SRM 482), the W-20Mo alloy (SRM 480), cartridge brass (SRM 478), and iron-3 percent silicon (SRM 483) were reevaluated with the new procedure. The homogeneity of RM 30, a set of glasses manufactured specifically for microhomogeneity, was also evaluated, as was a new issue of the iron-chromium-nickel alloys (SRM 479a).

Several of the samples above had been previously tested for homogeneity by the best methods available at that time. Rigorous evaluations were employed and gross inhomogeneities were readily detected by conventional ratemeter scans, TOPO, QRS, or random sampling. However, the extent of homogeneity, or inhomogeneity, is dependent upon the spatial definition of homogeneity and hence upon the method of measurement used in the testing procedure which should be chosen according to the purpose for which the material has been prepared. Micro-analytical techniques vary considerably in the amount of material sampled. EPMA was chosen to determine microhomogeneity because one can quantitate with the method and because a large number of micro samplings can be taken with reasonable ease. While such a refined determination of microhomogeneity would not be necessary when the material is used as a standard in spark source mass spectrometry (or optical emission spectroscopy), the information obtained is of considerable benefit to the understanding of material variability and how such variability could affect the measurement process.

We have now extended our ability to learn about these materials by using the new homogeneity testing procedure. With little trouble a material can be observed from micrometer to micrometer under complete automation. But just because we may now know more about this material does not mean that its quality as a microhomogeneity standard has changed. The new information should be helpful to the experimentalist in determining its usefulness in micro techniques.

Much of the following discussion is devoted to the steel standards (SRM 661-664). This is not because these materials are of any greater importance than the other materials that were tested; in fact, SRMs 661-664 were not specifically prepared for use as standards with EPMA. However, this is the first publication to include studies on the characterization of these standards while the other materials listed above were described in detail in previous publications [1-5,9,10]. Also, these steels are good examples for demonstrating the

microhomogeneity test procedure that we have developed. They have several added elements distributed between two phases and several types of inclusions. The discussion below shows how these materials can be used as standards even though a minor degree of inhomogeneity can be demonstrated.

Unless otherwise stated, experimental homogeneity scans were performed by moving the sample in 1 μm steps under a 1 μm -diameter electron beam. The computer program used in the statistical evaluation allowed for 50 steps per scan; therefore, each scan was 50 μm long. Counts were accumulated for ten seconds per reading. Two readings were taken on each step. The counts from each 10-s counting period were printed on a teletype. As many as three elements were simultaneously investigated. The specimen current was also recorded for each 10-s interval; this allowed easy observation of instrument drift. Unless otherwise stated, all homogeneity tests were made according to the above conditions.

For comparison, after each homogeneity test scan was prepared, data were collected with the sample stationary. To simulate a scan of a homogeneous target, 100 10-s readings were recorded for the same area. Usually a 20 μm diameter electron beam was employed to avoid sample contamination and to approach the value corresponding to the average composition.

As long as there is no significant drift, the statistics from the stationary scan reflect only the counting statistics and small random instrumental errors. The results should be equivalent to what one would observe for a truly homogeneous sample. The comparison of the statistics on the moving sample to those of the stationary sample can therefore reveal the homogeneity or inhomogeneity of the specimen. For all stationary scans both the "within" and "between" components of the standard deviation were small and in agreement with that predicted from counting statistics only. The results of stationary scans are not included in the following tables of results as they were primarily used to verify that the larger standard deviations observed in the test scans of the moving sample were indeed due to inhomogeneity and not to large instrumental errors.

For samples that were homogeneous, i.e., within the ± 3 -sigma limits predicted from Poisson statistics, a periodic ratemeter scan was all that was needed to define the homogeneity. In the few cases where the statistical evaluation was also done on apparently homogeneous materials, the standard deviations, including the "between" component, were very small. But in the cases which appeared to be inhomogeneous in the ratemeter scans, a large "between" component of the standard

deviation was obtained in the analysis of variance. The magnitude of this component depended upon the degree of inhomogeneity in the scanned region.

In the following discussions of the results there are several tables of statistical results. The standard deviations cited therein are not certified values because we have no proof at present that the micro-inhomogeneity is sufficiently uniform within each batch of specimens that its numerical expression can be guaranteed for the entire batch. The numbers given are only an approximate estimate of the inhomogeneity one can expect from a particular element in a given SRM. The estimates were calculated from only one 50 μm scan on only one sample. Although the homogeneity procedure has been considerably simplified, it would be an onerous task to provide a certified value defining the extent of inhomogeneity even if the batches were of uniform homogeneity. To do this for each element, several 50 μm scans on several samples of the same standard would be needed.

We therefore provide only a rough estimate of inhomogeneity to the users of these SRMs. If the user finds it necessary to apply any of these materials which were found to be inhomogeneous as standards, we advise that he determine the "within" and "between" components of variance of his measurements from his own SRM samples. This can be easily done by taking many random readings from the sample and calculating the components from the equations in Appendix 10.

Iron and Steel SRMs 661, 662, 663, 664

The certificates for these SRMs are shown in Appendix 1. The concentrations were obtained by analysis of the bulk sample. Although these standards have numerous inclusions, they can be used in microanalyses for those elements which are not preferentially concentrated in the inclusions, and are fairly homogeneously distributed throughout the metal matrix.

These steel SRMs had been previously studied in this laboratory [8] to determine the chemical compositions and distribution densities of the inclusions. The SRMs are in the form of rods 3.2 mm in diameter and 51 mm long. Polished mounts were prepared of cross sections (normal to the long axis) and of longitudinal sections (parallel to the axis). In these early studies, a large number of inclusions in each steel were qualitatively analyzed with the lithium-drifted silicon detector [Si(Li)] on the EPMA. To confirm the

results from the Si(Li) detector, wavelength scans of several inclusions in SRM 661 were recorded.

In the earlier studies, at least two types of inclusions were found in all steels - those with elements of average atomic number higher (high-Z) than the matrix and those with elements of average atomic number lower (low-Z) than the matrix. These classifications were made on the basis of the target current images, i.e., on whether the inclusions were lighter or darker than the matrix. The major constituents found in the high-Z inclusions in all steels were titanium, niobium, zirconium, and tantalum. This type of inclusion is probably what the metallurgist refers to as a refractory carbide. Some silicon was observed in the wavelength scans of such inclusions in SRM 661. If silicon were present in the high-Z inclusions in the other steels, it was obscured in the energy-dispersive spectra by the Ta $M\alpha$ peak and the Nb and Zr $L\alpha$ peaks. A small amount of silver was also found in the high-Z inclusions of SRM 664.

In SRMs 661, 662, and 663 most of the low-Z inclusions contained sulfur, manganese, and selenium. Oxygen, magnesium, aluminum, silicon, zirconium, niobium, and cerium were also found in the wavelength scans of such inclusions in SRM 661. These probably are another common type of inclusion generally referred to as "glassy", which contain oxides of silicon, aluminum, magnesium, and cerium and some sulphides, mainly manganese sulphide.

In all the steels some of the low-Z inclusions contained the same elements as the high-Z inclusions. It was concluded that these were probably holes which formed when part of the high-Z inclusion had been chipped out in the polishing procedure. Such holes would appear to be low-Z inclusions in the target current image.

The low-Z inclusions in SRM 664 were varied in composition. Some contained mostly iron with small amounts of molybdenum. Others were quite similar in composition to the matrix and contained also small amounts of sulfur, vanadium, and manganese.

Figures 7 to 9 show target current images and x-ray area scans of cross-sections of SRM 663 and SRM 664 and of a longitudinal section of SRM 662. In figure 7 the two types of inclusions are present in the target current image (a) of SRM 664. The low-Z inclusions appear as white spots and the high-Z inclusions are dark. X-ray area scans b, c, and d show that titanium, tantalum, and niobium are considerably more concentrated in the inclusions than in the matrix. Manganese and nickel (scans e and f respectively) show no

preferential enrichment in the inclusions; yet the manganese distribution appears to be spotty while that of nickel seems to be more evenly distributed.

In figure 8 the x-ray area scan of titanium (b) in SRM 663 shows that this element again is preferentially located in the low-Z inclusions. The x-ray area scan for vanadium (c) is spotty indicating inhomogeneity of this element.

Several of the inclusions in the longitudinal section (figure 9) form stringers (a). Zirconium (b) and again titanium (c) are present primarily in the inclusions.

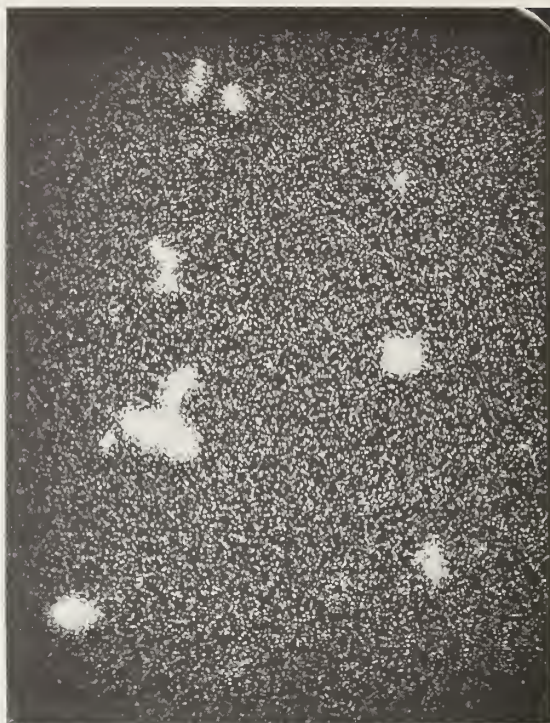
Regions of the main phase in SRMs 661-664 were tested for homogeneity. All scans were made at 30 KV with a beam current of approximately 1.5×10^{-7} A. The results of the statistical evaluations of these homogeneity scans are shown in Tables III thru VI. Two different samples of each steel were analyzed — a cross-section and a longitudinal section. All elements that exhibited a discernible signal above the baseline were tested in the cross-section scans. Only nickel and copper were tested in the longitudinal section.

In these tables the postulated mean concentrations are those taken from the SRM certificate (Appendix 1). \bar{X} is the average (in counts) of the 100 x-ray measurements (50 steps, each repeated once), and the background, \bar{B} , is an average of five readings taken from pure iron (rounded to the nearest 100).

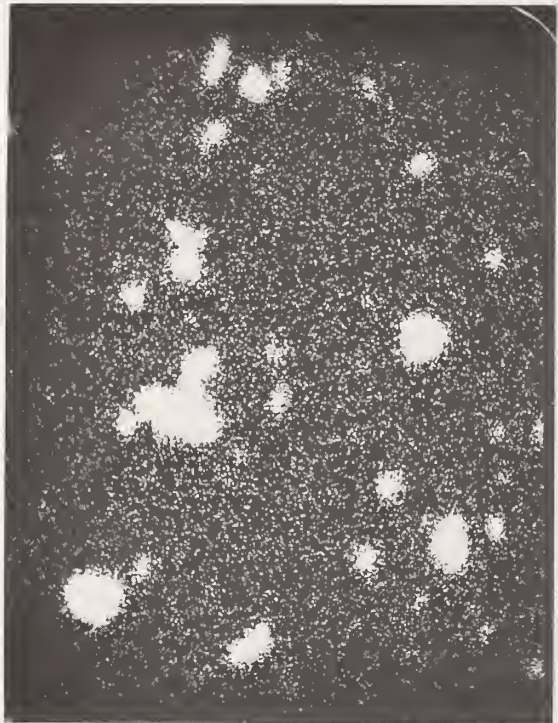
The estimated standard deviations (in counts), σ_W and σ_B are the "within" and "between" components respectively. The numbers in parentheses are the coefficients of variation (in percent), $\frac{100 \sigma_W}{\bar{X}}$ and $\frac{100 \sigma_B}{\bar{X}}$, respectively. The equations used to calculate σ_W and σ_B are numbers 2 thru 6 in Appendix 10. A comparison of σ_B with σ_W (in either counts or percent) gives a good indication of how inhomogeneous the element is in the sample.

The "between" standard deviation σ_B , in weight percent, represents the inhomogeneity component of the standard deviation in terms of concentration for a single measurement. It is a rough estimate calculated on the basis of a linear relationship between the number of counts and the concentration. The equation used is

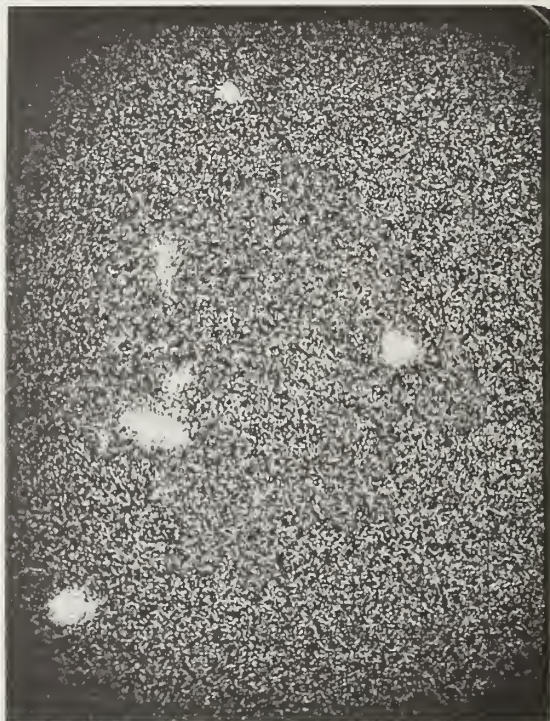
d



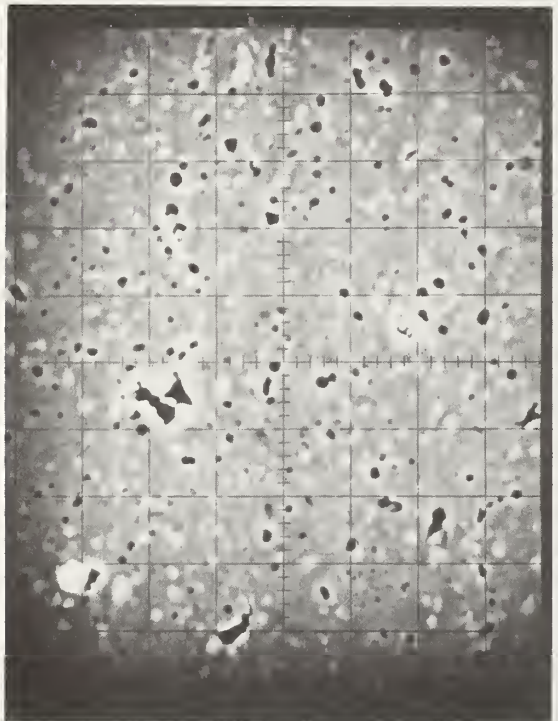
b

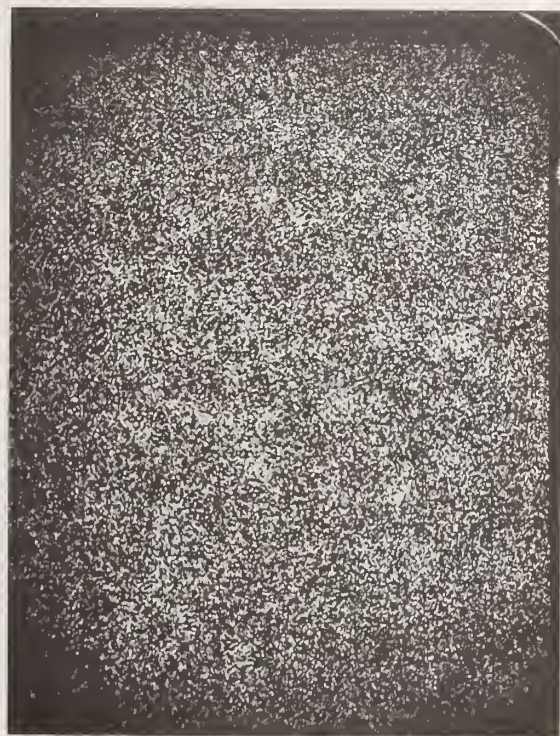


c

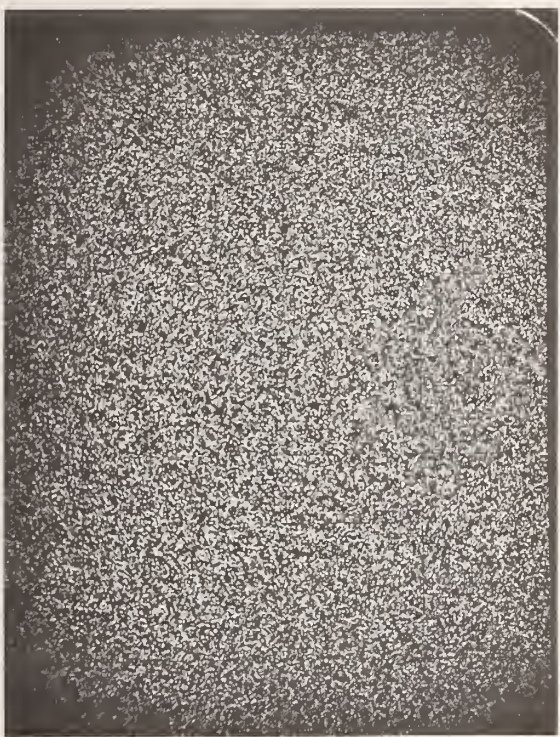


a





e



f

Figure 7. Cross-section of SRM 664. Area = $80 \times 100 \mu\text{m}^2$, 30 kV, 9×10^{-8} A beam current.

- a. target current image; b. x-ray area scan of titanium;
- c. x-ray area scan of tantalum; d. x-ray area scan of niobium;
- e. x-ray area scan of manganese; f. x-ray area scan of nickel.

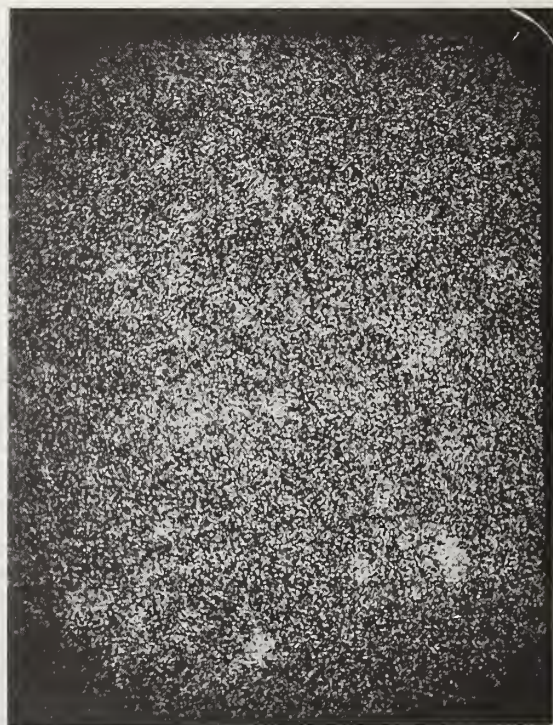
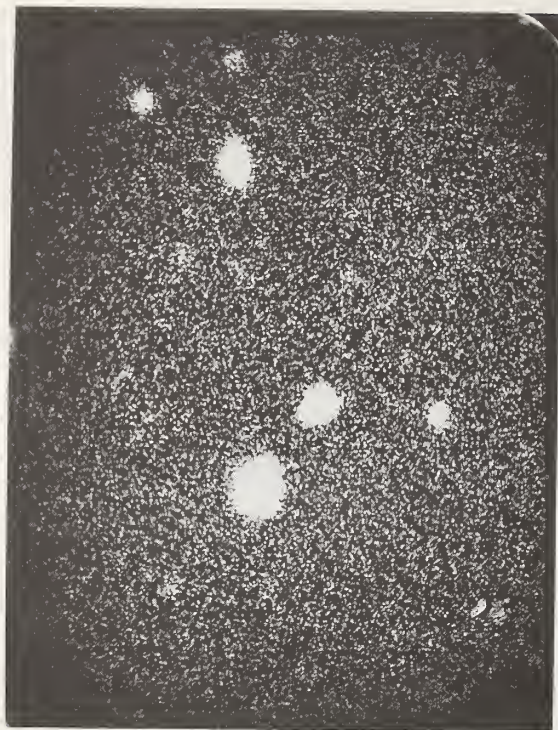
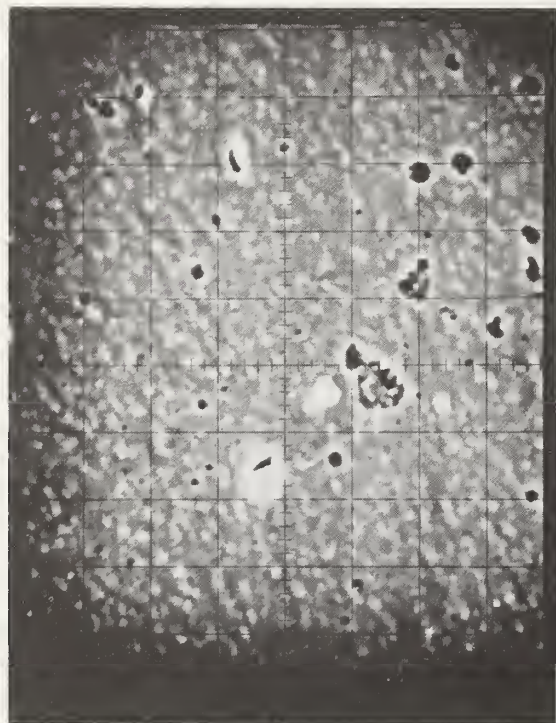


Figure 8.

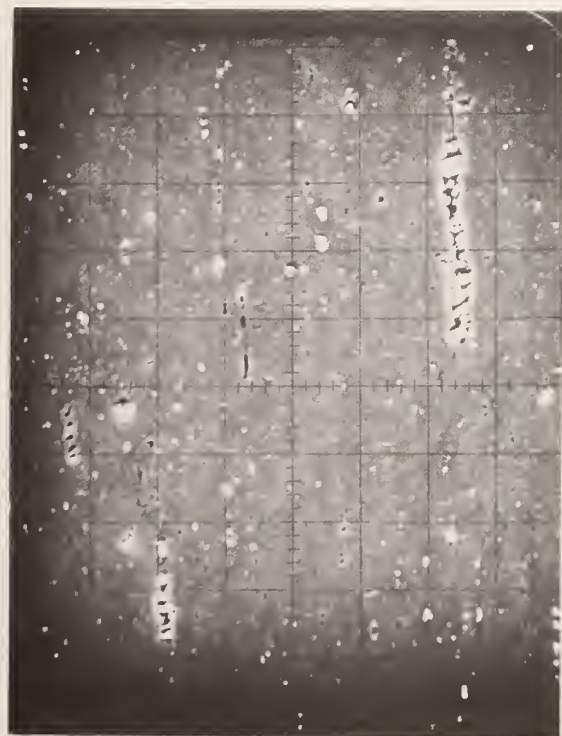
Cross-section of SRM 663.

Area = $80 \times 100 \mu\text{m}^2$, 30 kV,
 9×10^{-8} A beam current.

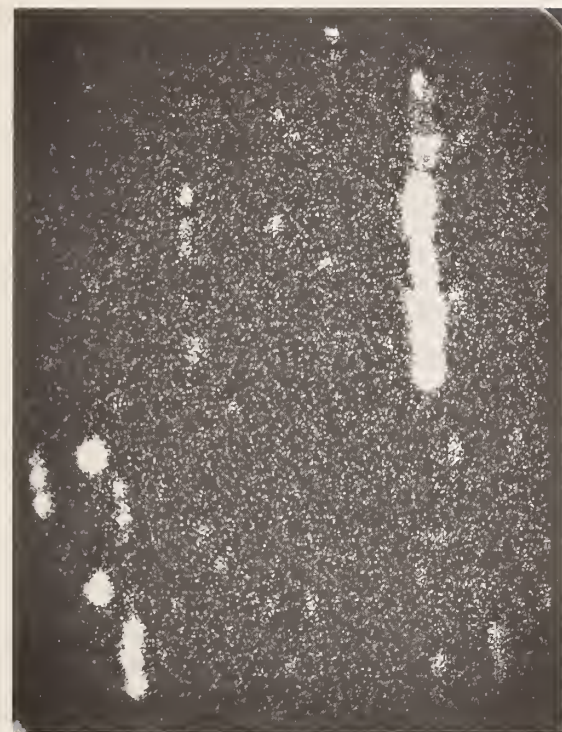
a. target current image,

b. x-ray area scan of titanium,

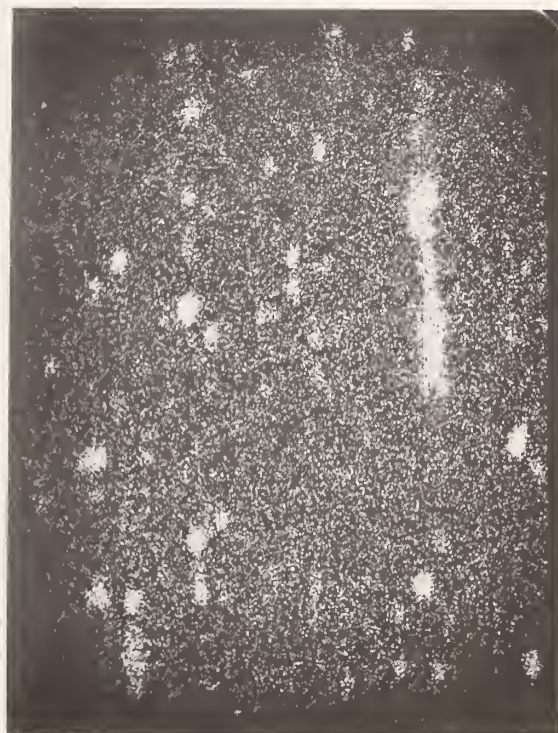
c. x-ray area scan of vanadium.



a



b



c

Figure 9. Longitudinal cross-section of SRM 662. Area = $160 \times 200 \mu\text{m}^2$, 9×10^{-8} A beam current.

- a. target current image;
- b. x-ray area scan of zirconium;
- c. x-ray area scan of titanium.

$$\hat{\sigma}_B(\text{in wt. \%}) = \hat{\sigma}_B(\text{in counts}) \times \frac{\text{concentration (wt. \%)}}{\bar{X} - \bar{B}} \quad (1)$$

This value is strictly valid for the measured standard specimen only. It is not intended to be used for accurate work with another piece of the same SRM; rather, it is meant to provide a rough estimate of the affect of inhomogeneity when the SRMs tested here are used as standards in other laboratories and where the necessary accuracy does not warrant that the experimentalist redetermine the inhomogeneity of his particular standard material specimen. Once $\hat{\sigma}_W(\text{in wt\%})$ is obtained (from several duplicate readings), it can be combined with $\hat{\sigma}_B(\text{in wt\%})$ and with the uncertainty in the mean concentration from the certificate (U_1 , in wt%) to obtain a fair estimate of the total uncertainty, U , in terms of concentration as derived from the intensity measurements. See equation 10 in Appendix 10.

In Tables III thru VI, the uncertainty of the electron probe measurement CU_2 , combines the "within" and "between" components of variance with the contribution from the background measurement. U is the total uncertainty (99.7% confidence level) in the estimate of concentration obtained by combining CU_2 and U_1 . The equations used for estimating these uncertainties are in Appendix 10.

The elements tested in the four steels were those which are primarily located in the main phase. Exceptions to this were manganese and titanium. Manganese appears to be located throughout both the main phase and the inclusions with apparently no strong preference for either. This can be observed in the area scans (see figure 7e). But titanium, though present in both phases, shows a strong preference for the inclusions (see figures 7b, 8b, and 9c). This preference alone precludes the use of these SRMs as micro standards for titanium in steel. The results of titanium measurements were included here only to show how the magnitude of the $\hat{\sigma}_B$ reveals that the element is grossly inhomogeneous.

In a few cases the signal above the background is not large (only a few hundred counts). Such is the case for copper in SRMs 661 and 663, vanadium in SRM 662, and tungsten in SRM 664. The relative values for $\hat{\sigma}_W$ could, in these situations, be largely due to poor counting statistics only. Therefore, one cannot draw any conclusions regarding homogeneity when counting statistics are poor.

Table III. Homogeneity Study of SRM 661.

Sample ^a	Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^b$	Counts	$\hat{\sigma}_B^b$	wt. %	Uncertainties (in wt %) ^c		
									cU ₂	U ₁	U
1	CrK α	0.69	18676	1900	$\pm 303(1.6)$	$\pm 2709(14.5)$	± 0.11		± 0.047	± 0.005	$\pm 0.048(7.0)$
	MnK α	0.66	5831	1000	$\pm 97(1.7)$	$\pm 606(10.4)$	± 0.083		± 0.036	± 0.010	$\pm 0.037(5.6)$
	NiK α	1.99	23300	2600	$\pm 154(0.7)$	$\pm 348(1.5)$	± 0.033		± 0.016	± 0.010	$\pm 0.019(1.0)$
	CuK α	0.042	2298	2000	$\pm 44(1.9)$	$\pm 22(1.0)$	± 0.0030		± 0.009	± 0.001	$\pm 0.009(21)$
2	NiK α	1.99									
	scan I		31914	3300	$\pm 225(0.7)$	$\pm 764(2.4)$	± 0.053		± 0.024	± 0.010	$\pm 0.026(1.3)$
	scan II		31425	3300	$\pm 217(0.7)$	$\pm 824(2.6)$	± 0.058		± 0.026	± 0.010	$\pm 0.028(1.4)$
	CuK α	0.042									
	scan I		2631	2300	$\pm 50(1.9)$	$\pm 0(0)$	-		± 0.008	± 0.001	$\pm 0.008(19)$
	scan II		2619	2300	$\pm 55(2.1)$	$\pm 13(0.5)$	± 0.0017		± 0.009	± 0.001	$\pm 0.009(21)$

^aSample 1 is a cross-section; sample 2 is a longitudinal section.^b $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{\bar{X}}$.^cSee Appendix 10 for definitions of symbols.

Table IV. Homogeneity Study of SRM 662.

Sample ^a	Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^b$		$\hat{\sigma}_B^b$		Uncertainties (in wt %) ^c		
									cU_2	U_1	U
1	CrK α	0.30	4769	1000	$\pm 105(2.2)$		$\pm 599(12.6)$		± 0.021	± 0.010	$\pm 0.023(7.7)$
	MnK α	1.04	7559	800	$\pm 122(1.6)$		$\pm 560(7.4)$		± 0.037	± 0.010	$\pm 0.039(3.8)$
	NiK α	0.59	9943	3000	$\pm 103(1.0)$		$\pm 200(2.0)$		± 0.010	± 0.010	$\pm 0.014(2.4)$
	CuK α	0.50	4209	2000	$\pm 68(1.6)$		$\pm 152(3.6)$		± 0.020	± 0.010	$\pm 0.023(4.6)$
	TiK α	0.84	1778	900	$\pm 137(7.7)$		$\pm 1295(72.8)$		± 0.529	± 0.001	$\pm 0.529(6.3)$
	VK α	0.41	913	650	$\pm 32(3.5)$		$\pm 57(6.3)$		± 0.067	± 0.005	$\pm 0.067(16)$
	CoK α	0.30	12433	6300	$\pm 111(0.9)$		$\pm 117(0.9)$		± 0.006	± 0.010	$\pm 0.012(4.0)$
	NiK α	0.59									
2	scan I		11441	3300	$\pm 97(0.85)$		$\pm 216(1.9)$		± 0.009	± 0.010	$\pm 0.013(2.2)$
	scan II		11568	3300	$\pm 112(0.97)$		$\pm 101(0.87)$		± 0.007	± 0.010	$\pm 0.012(2.0)$
	CuK α	0.50									
	scan I		5021	2300	$\pm 74(1.5)$		$\pm 209(4.2)$		± 0.021	± 0.010	$\pm 0.023(4.6)$
	scan II		5146	2300	$\pm 107(2.1)$		$\pm 355(6.9)$		± 0.029	± 0.010	$\pm 0.031(6.2)$

^aSample 1 is a cross-section; sample 2 is a longitudinal section.^b $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{\bar{X}}$.^cSee Appendix 10 for definitions of symbols.

Table V. Homogeneity Study of SRM 663.

Sample ^a	Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^b$	Counts	$\hat{\sigma}_B^b$	wt. %	Uncertainties (in wt %) ^c		
									cU ₂	U ₁	U
1	CrK α	1.31	9770	650	$\pm 213(2.2)$	$\pm 1757(18)$	± 0.25		± 0.108	± 0.010	$\pm 0.108(8.2)$
	MnK α	1.50	7296	950	$\pm 145(2.0)$	$\pm 780(11)$	± 0.18		± 0.079	± 0.018	$\pm 0.081(5.0)$
	NiK α	0.32	6958	3000	$\pm 88(1.3)$	$\pm 115(1.7)$	± 0.009		± 0.007	± 0.010	$\pm 0.012(3.8)$
	CuK α	0.098	2577	2000	$\pm 45(1.7)$	$\pm 18(0.7)$	± 0.003		± 0.011	± 0.005	$\pm 0.012(12)$
	TiK α	0.05	1619	900	$\pm 51(3.1)$	$\pm 591(37)$	± 0.041		± 0.018	± 0.001	$\pm 0.018(36)$
	VK α	0.31	2860	650	$\pm 77(2.7)$	$\pm 335(11.7)$	± 0.047		± 0.021	± 0.010	$\pm 0.023(7.4)$
2	NiK α	0.32									
	scan I		7926	3300	$\pm 89(1.1)$	$\pm 161(2.0)$	± 0.011		± 0.007	± 0.010	$\pm 0.012(3.8)$
	scan II		7928	3300	$\pm 99(1.3)$	$\pm 197(2.5)$	± 0.014		± 0.008	± 0.010	$\pm 0.013(4.1)$
	CuK α	0.098									
	scan I		2926	2300	$\pm 48(1.6)$	$\pm 26(0.9)$	± 0.004		± 0.010	± 0.005	$\pm 0.012(12)$
	scan II		2925	2300	$\pm 54(1.9)$	$\pm 10(0.4)$	± 0.002		± 0.010	± 0.005	$\pm 0.012(12)$

^aSample 1 is a cross-section; sample 2 is a longitudinal section.^b $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{\bar{X}}$.^cSee Appendix 10 for definitions of symbols.

Table VI. Homogeneity Study of SRM 664.

Sample ^a	Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^b$	Counts	$\hat{\sigma}_B^b$	wt. %	Uncertainties (in wt %) ^c
									cU_2 U_1 U
1	CrK α	0.07	2258	1100	$\pm 43(1.9)$	$\pm 185(8.2)$	± 0.011	± 0.006	± 0.005 $\pm 0.007(10)$
	MnK α	0.26	2816	1000	$\pm 55(1.9)$	$\pm 403(14)$	± 0.058	± 0.025	± 0.005 $\pm 0.026(10)$
	NiK α	0.14	4565	3000	$\pm 70(1.5)$	$\pm 199(4.4)$	± 0.018	± 0.010	± 0.005 $\pm 0.011(7.9)$
	CuK α	0.25	3218	2000	$\pm 53(1.7)$	$\pm 119(3.7)$	± 0.024	± 0.016	± 0.005 $\pm 0.017(6.8)$
	TiK α	0.24	2986	900	$\pm 177(5.9)$	$\pm 3235(108)$	± 0.372	± 0.158	± 0.010 $\pm 0.158(66)$
	VK α	0.11	1328	600	$\pm 41(3.1)$	$\pm 287(22)$	± 0.043	± 0.019	± 0.005 $\pm 0.020(18)$
	CoK α	0.15	9616	6600	$\pm 91(.95)$	$\pm 340(3.5)$	± 0.017	± 0.009	± 0.010 $\pm 0.014(9.3)$
	MoL α	0.49	1187	700	$\pm 54(4.5)$	$\pm 396(33)$	± 0.398	± 0.174	± 0.010 $\pm 0.174(36)$
	WL α	0.10	4622	4400	$\pm 69(1.5)$	$\pm 89(1.9)$	± 0.040	± 0.044	± 0.005 $\pm 0.045(45)$
	NiK α	0.14							
2	scan I		5231	3300	$\pm 74(1.4)$	$\pm 148(2.8)$	± 0.011	± 0.007	± 0.005 $\pm 0.009(6.4)$
	scan II		5016	3300	$\pm 70(1.4)$	$\pm 273(5.5)$	± 0.022	± 0.011	± 0.005 $\pm 0.013(9.3)$
	CuK α	0.25							
	scan I		3719	2300	$\pm 70(1.8)$	$\pm 115(3.1)$	± 0.020	± 0.015	± 0.005 $\pm 0.016(6.4)$
	scan II		3540	2300	$\pm 68(1.9)$	$\pm 257(7.3)$	± 0.052	± 0.026	± 0.005 $\pm 0.026(10)$

^aSample 1 is a cross-section; sample 2 is a longitudinal section.^b $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{\bar{X}}$.^cSee Appendix 10 for definitions of symbols.

Only nickel and copper were tested in the longitudinal sections. These two elements appeared to be reasonably homogeneous in the cross-section scans. Also, nickel is expected to be homogeneous as in principle it is completely soluble in the iron matrix. Scan I of the longitudinal section was parallel to the length of the rod from which the standard pieces were sectioned, while scan II was perpendicular to it. Scan II is essentially a cross section scan. The results of the measurements for nickel and copper in both samples are comparable.

As previously discussed, other laboratories wishing to use these SRMs for micro standards may wish to evaluate the homogeneity of their specimen of the standard reference material. The easiest and least time-consuming way to do this is by random sampling. To check the validity of such a procedure, we determined the error due to inhomogeneity obtained to random sampling for three elements in our four specimens and compared this error to the "between" component of the standard deviation.

Nickel, chromium, and manganese were measured in the four SRMs. A 1 μ m beam was used at 30KV and a beam current of slightly less than 1.5×10^{-7} A. Counting periods were 10s. Data were taken from ten randomly chosen points on the specimen avoiding all visible inclusions. Each specimen was used twice in the experiment; therefore, two independent standard deviations were calculated for each element and SRM. Equation (1) was used to calculate these standard deviations in weight percent (σ_B (in wt%)). In Table VII they are compared to σ_B (in wt%) obtained from the homogeneity traces (Tables V through VII). In most cases σ_B (in wt%) calculated from random sampling agrees quite well with that calculated from the homogeneity traces.

Generally, a particular level of precision for the measurement process is desired. This generally can be met by taking the appropriate number of random samples, n . The standard deviation of a single point, as determined alone, multiplied by $n^{-1/2}$ is an estimate of the standard deviation of the average of n measurements. One, therefore, can pre-determine how many measurements must be made to meet the desired precision. Such a procedure should, however, be interpreted with caution. It implies, among other things, that the subsample (specimen) used by the analyst does not differ significantly in composition from the portions which were used in chemical analysis.

Table VII. Comparison of Random Sampling with Homogeneity Traces for Iron and Steel SRMs.

Sample			Element		
			Ni	Cr	Mn
661	Conc (wt%)		1.99	0.69	0.66
	σ_B (wt%)	RS ^a	0.046	0.120	0.089
		RS _b	0.041	0.093	0.067
		HT ^b	0.034	0.110	0.083
662	Conc (wt%)		0.59	0.30	1.04
	σ_B (wt%)	RS	0.021	0.045	0.087
		RS	0.018	0.040	0.089
		HT	0.017	0.048	0.086
663	Conc (wt%)		0.32	1.31	1.50
	σ_B (wt%)	RS	0.014	0.110	0.075
		RS	0.011	0.198	0.155
		HT	0.009	0.250	0.180
664	Conc (wt%)		0.14	0.07	0.26
	σ_B (wt%)	RS	0.024	0.021	0.101
		RS	0.020	0.028	0.064
		HT	0.018	0.011	0.058

^aRS = Random Sampling.

^bHT = Homogeneity Trace.

In conclusion, there are few elements in these samples which are close to being homogeneously distributed on the micrometer scale. Any use of these SRMs as micro standards in quantitative analyses must be done with great caution. Our estimates of inhomogeneity should only be applied to other specimens of the standards when high accuracy is not needed. To improve the accuracy of analysis, one should redetermine the inhomogeneity of one's own piece by taking many random samplings and applying the equations in Appendix 10. The larger the number of samplings taken, the more accurate will be the estimate of inhomogeneity, and of the x-ray intensity which corresponds to the nominal average composition of the standard.

Low-Alloy Steel SRMs 461 and 463

These SRMs were previously tested for homogeneity [1,2]. The overall compositions of these samples appear in the Provisional Certificate of Analysis in Appendix 2.

In the first homogeneity study of SRM 461, chromium, silicon, and manganese were found at high levels in the inclusions. Nickel and iron were reported to be homogeneous throughout the matrix. This was determined from numerous random samplings with a 2-4 μm diameter electron beam.

Sulphur, zirconium, niobium, and tantalum were found in the inclusions of SRM 463. Manganese was determined to be inhomogeneously distributed throughout the matrix while iron, copper, nickel, and silicon were found to be homogeneous at the 3 μm level.

In the present work, homogeneity test scans were prepared for nickel, copper, molybdenum, and cobalt in SRM 461 and for silicon, nickel, copper, and vanadium in SRM 463. The results appear in Table VIII. Only the nickel in SRM 461 shows a high signal above the background level. Since $\hat{\sigma}_B$ is more than three times $\hat{\sigma}_W$, nickel is probably somewhat inhomogeneously distributed throughout this sample. The homogeneity of the other three elements could not be determined since the signals are low in these cases. In SRM 463, nickel again appears to be inhomogeneous, as does vanadium. But silicon and copper appear to be more homogeneous.

Gold-Silver and Gold-Copper Wires, SRMs 481 and 482

The certificates for the gold-silver (SRM 481) and the gold-copper alloys (SRM 482) are shown in Appendices 3 and 4. The original criterion for acceptable homogeneity of these samples was that the maximum composition variations should not exceed .01 (mass-fraction). The data quoted in the certificate indicate that this criterion was met. The original homogeneity test was made with TOPO (5).

We retested these samples for homogeneity with the new procedure. Two scans perpendicular to each other were made for each of two samples of each wire. The sample was moved in 1 μm steps under a 1 μm diameter electron beam for a length of 100 μm . The periodic ratemeter traces of these scans were within the limits of ± 3 -sigma calculated from Poisson counting statistics and within 1 percent. Therefore, these samples are considered satisfactorily homogeneous.

Table VIII. Homogeneity Study of Low-Alloy Steel SRMs 461 and 463.

Sample	Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^a$	Counts	$\hat{\sigma}_B^a$	wt. %	cU_2 (in wt. %) ^b
461	NiK α	1.73	12056	1800	$\pm 116(1.0)$	$\pm 376(3.1)$		± 0.063	± 0.029
	CuK α	0.34	3783	3200	$\pm 53(1.4)$	$\pm 24(0.6)$		± 0.014	± 0.046
	MoK α	0.30	1045	700	$\pm 40(3.9)$	$\pm 29(2.8)$		± 0.020	± 0.034
	CoK α	0.26	3243	2700	$\pm 52(1.6)$	$\pm 77(2.4)$		± 0.037	± 0.038
463	SiK α	0.41	1085	350	$\pm 29(2.7)$	$\pm 17(1.6)$		± 0.009	± 0.015
	NiK α	0.39	3746	1800	$\pm 56(1.5)$	$\pm 145(3.9)$		± 0.029	± 0.017
	CuK α	0.47	3859	3200	$\pm 56(1.4)$	$\pm 77(2.0)$		± 0.055	± 0.060
	VK α	0.10	1432	600	$\pm 45(3.2)$	$\pm 123(8.6)$		± 0.015	± 0.008

^a $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{X}$

^bOnly a Provisional Certificate of Analysis has been issued for these SRMs and the uncertainties for the chemical analysis (U_1) are not available. As seen in Tables V-VIII, U_1 has little or no effect on cU_2 when calculating U . Therefore, cU_2 can validly be assumed here to be the same as U . See Appendix 10 for definition of symbols.

Statistical evaluations with the computer programs were not done for most of these samples. Experience has shown that if a ratemeter trace looks satisfactory, i.e., all or most readings fall within the ± 3 -sigma limits, the calculated standard deviations will be small.

One homogeneity scan was statistically evaluated for a Au80-Cu20 sample. This was a 50 μm scan with a 1 μm diameter beam stepping across the sample in 1 μm steps, each repeated once. The statistical results which appear in Table IX show no evidence of inhomogeneity.

Tungsten-20 Molybdenum Alloy, SRM 480

This SRM was previously tested for homogeneity in 1968 by the QRS procedure [3]. A total of 100 points were tested in a 10 x 10 point matrix 48 μm along each edge. Four to five rasters in each of three samples were tested. The overall coefficient of variation was determined to be 2.5 percent for molybdenum and 1.5 percent for tungsten. The certificate for this SRM is in Appendix 5.

The usual homogeneity scan of one specimen using 1 μm steps across 50 μm in the sample interior showed a portion of a wavy, continuous signal. While the counts for one component increased, the counts for the other decreased. The deviations from the average number of counts were outside the Poisson ± 3 -sigma limits. The first few scans of this type indicated that these "waves" extended well beyond 50 μm . Thus, scans over longer distances were needed. In the QRS procedure used previously this type of trend could have been missed.

Subsequent scans of 1 μm steps across 250 μm confirmed the above results and showed that the fluctuations or waves are not periodic. Finally three scans were made across the same specimen in 10 μm steps from edge to edge. Each scan was approximately 60° from the previous. Figure 10 illustrates one of these scans. The ± 3 -sigma limits about the average are indicated by double-headed arrows. The regions beyond the dashed lines at the beginning and end of the scan correspond to the extreme edges of the sample which, as previously suggested [3], should be avoided when using this standard.

In figure 10 the concentration change represented by a signal fluctuation from a maximum to a minimum is approximately 3 weight percent. If the statistics found previously [3] are applied to this trace, most points fall within the ± 3 -sigma limits. The 2.5 percent coefficient of variation for molybdenum is equivalent to ± 0.53 weight percent or a ± 3 -sigma of ± 1.59 weight percent. And for tungsten the 1.5 percent coefficient of variation is equivalent to a ± 3 -sigma of ± 3.6 weight percent.

Table IX. Homogeneity Study of Gold-Copper Alloy SRM 482.

Element and X-ray Line	Conc. in wt. %	\bar{X}	\bar{B}	$\hat{\sigma}_W^a$		Counts	$\hat{\sigma}_B^a$		Uncertainties (in wt %) ^b	
									CU_2	U_1 U
AuM α_1	80.20	28328	1000	$\pm 166(0.6)$		$\pm 91(0.3)$	± 0.27		± 0.223	± 0.10 $\pm 0.244(0.3)$
CuK α	19.80	28731	1000	$\pm 224(0.8)$		$\pm 0(0.0)$	0.0		± 0.063	± 0.10 $\pm 0.118(0.6)$

^a $\hat{\sigma}_W$ and $\hat{\sigma}_B$ are expressed as percent in parentheses = $\frac{100\hat{\sigma}}{\bar{X}}$

^bSee Appendix 10 for definitions of symbols.

NBS SRM 480, Tungsten-20 Molybdenum Alloy

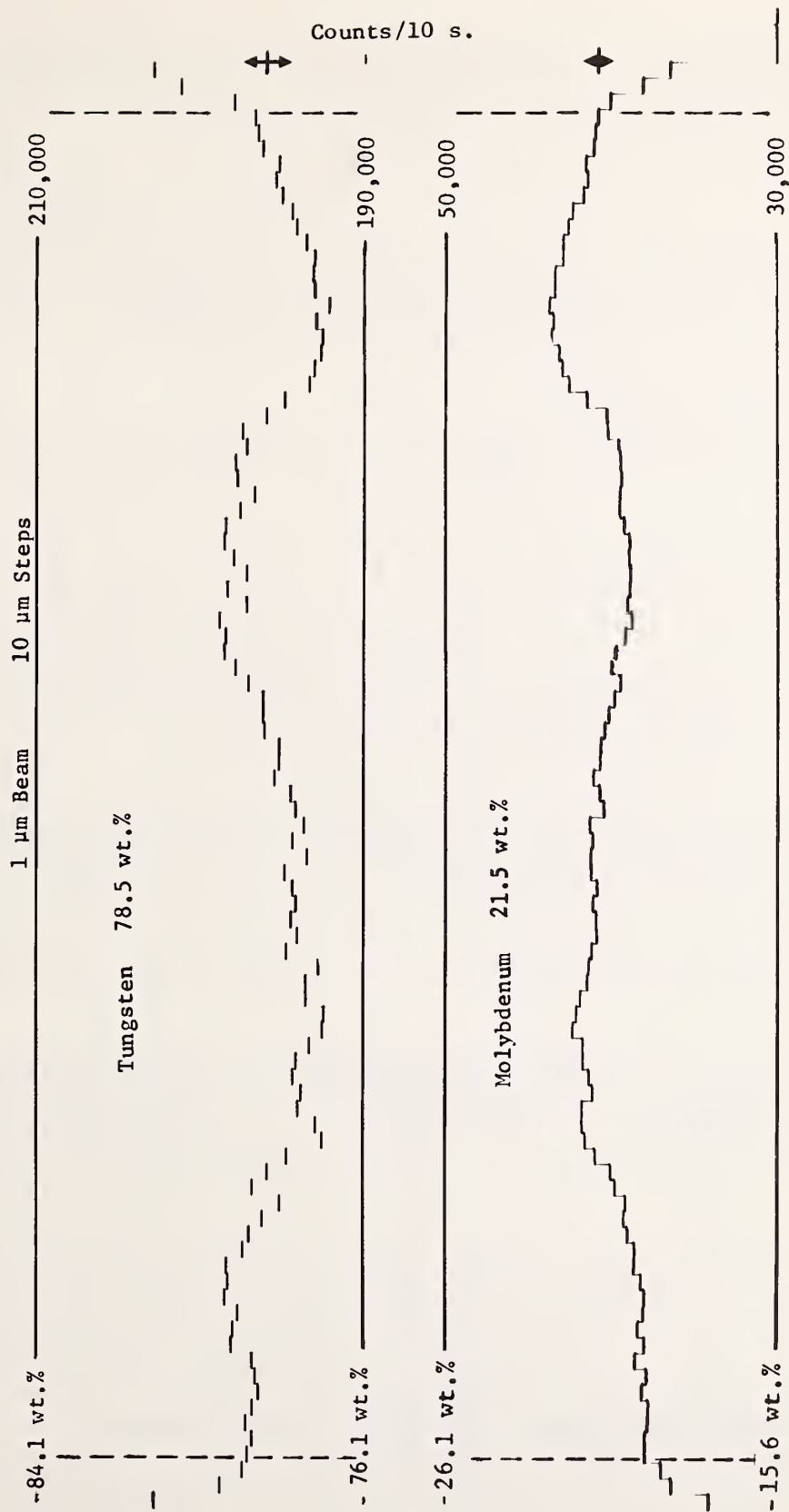


Figure 10. Periodic integrator homogeneity trace of tungsten and molybdenum simultaneously recorded from SRM 480. Traverse crosses the sample from edge to edge in 10 μm steps with a 1 μm electron beam.

Statistical evaluations with the Paule program were not made of these scans. The equations used in this program are based on random distribution models and they do not apply to the type of trends that we are observing here.

The other two scans of this specimen are similar to figure 10. One scan shows only one maximum and minimum near the beginning of the trace with very little change across the second half of the scan. Such anomalies and lack of consistency reinforces the need for taking many randomly selected samples when using this specimen as a standard.

Cartridge Brass, SRM 478

The certificate for SRM 478 is in Appendix 6. This SRM consists of two forms - wrought (NBS-1102) and cast (NBS-C1102).

SRM 478 was one of the first NBS reference materials tested for microhomogeneity [2]. The random sampling technique with a 1 μ m electron beam was used to observe the major components, copper and zinc. Twenty-four random analytical points were used to test the wrought form; forty-two were used to test the cast form. To check reproducibility, a duplicate reading was taken at each test point.

The results of this early work are in Table X. The wrought form of the brass was found to be less homogeneous than the cast form, but none of the errors were so prohibitively large as to prevent the use of this SRM as a microstandard.

Table X. Homogeneity Testing of Cartridge Brass SRM 478.^a

<u>Sample</u>	<u>Element</u>	<u>Standard Deviation (%) Computed from Experiment</u>	<u>Analytical Range (two standard deviations in wt%)</u>
NBS-C1102	Cu	0.72	71.8 to 73.8
	Zn	0.79	26.7 to 27.5
NBS-1102 (wrought)	Cu	1.0	71.1 to 74.6
	Zn	2.2	25.9 to 28.3

^aData taken from reference (2).

In our present work, two pieces of the wrought form and two pieces of the cast form were studied. For each piece, two periodic ratemeter traces normal to one another were prepared. The sample was moved in $5\text{ }\mu\text{m}$ steps under a $1\text{ }\mu\text{m}$ electron beam. The probe was operated at 30 KV with a $1.5 \times 10^{-7}\text{ A}$ beam current.

A periodic integrator trace of copper and zinc in one of the wrought samples is in figure 11. This homogeneity trace is typical of those observed for all samples. The composition of these elements changes in a wave-like manner across the samples. The waves are not periodic; those in close proximity are about $125\text{ }\mu\text{m}$ from peak to valley but most waves stretch out over longer distances. Of the four traces prepared from the wrought sample, the largest concentration difference between a minimum and maximum was equivalent to 1.7 weight percent. For the cast samples the largest concentration fluctuation was 1.4 weight percent. These variations are within the deviations found previously (Table X).

Iron-Three Percent Silicon, SRM 483

This SRM was previously certified for microhomogeneity (see Appendix 7). The original testing was done on six different samples of the material [9]. Quantitative area scanning was used with a square matrix of 20×20 points covering an area of about one square millimeter. The use of the lithium-drifted silicon detector made it possible to study such a large area without defocusing problems. Statistical and spacial analysis was done with TOPO. From a total of 3700 individual analytical points, a conservative estimate of the coefficient of variation was determined to be one percent for the entire group of samples.

In the present work, homogeneity traces of iron and silicon were prepared at 20 KV with a $1.5 \times 10^{-7}\text{ A}$ beam current. The sample was moved in $5\text{ }\mu\text{m}$ steps under a $1\text{ }\mu\text{m}$ electron beam. Counting periods were 10s. These traces were made both along the longest dimension and normal to the longest dimension of two different pieces of this SRM.

The traces along the sample length covered a distance of about 1.5 mm. Some upward drift in the iron and silicon signals occurred which could only be attributed to a positive beam current drift. For both samples, most of the signal fluctuations fell within the ± 3 -sigma limits. One sample showed a short wave-like fluctuation for iron over about $50\text{ }\mu\text{m}$ where the peaks and valleys fell slightly outside the ± 3 -sigma limits. Such a fluctuation is still within the 1 percent coefficient of variation quoted in the certificate for microhomogeneity. The iron signal showed greater random

SRM 478

CARTRIDGE BRASS

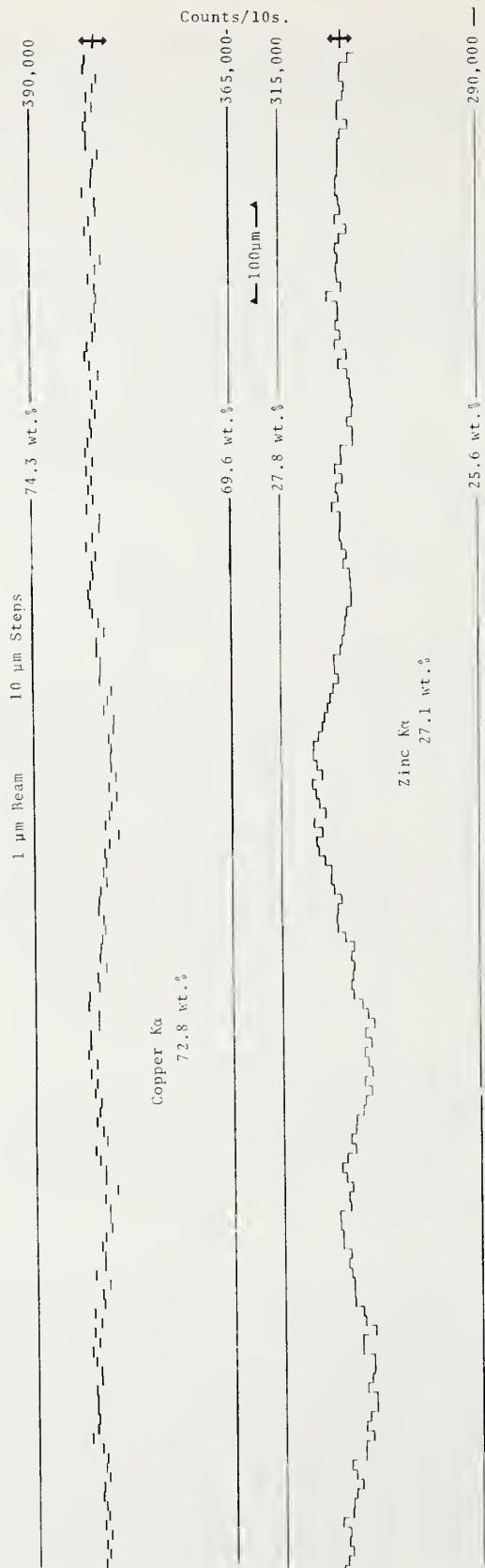


Figure 11. Periodic integrator homogeneity trace of zinc and copper simultaneously recorded from NBS SRM 478 Cartridge Brass (voltage = 30kV, beam current = 1.5×10^{-7} A). The sample was advanced in 5 μm steps under a 1 μm electron beam after each ten-second counting period.

variations in the scans that were made normal to the longest dimension than in those run along the longest dimension. The signal often falls outside the ± 3 -sigma limits, but again not so far as to exceed the 1 percent certificate limits. In all homogeneity traces, the silicon signal is within the ± 3 -sigma limits.

Glasses for Microanalysis, RM-30

A list of ten glasses that make up this NBS Research Material Set appears in Appendix 8. The nominal compositions are listed; they were calculated from the weight of material added to the melt. These Research Materials were prepared to fulfill a need for standards containing low concentrations of many different elements. Glasses were selected as the matrix material because they can easily meet the microhomogeneity requirement and because most metal oxides can easily be added to glasses in small quantities.

Except for the Al_2O_3 - B_2O_3 glasses, homogeneity traces were prepared for the major constituents of the glasses. Scans were run on two different pieces of each glass at 15 KV with a beam current of about 7.5×10^{-8} A. A 1 μm electron beam was used while moving the sample in 1 μm steps under the beam for 10-s counting periods. The traces are in figures 12 through 15, where the scan across the moving sample is to the right and the trace with the stationary 20 μm beam is to the left. Deviations are within the ± 3 -sigma limits. The traces contain no evidence of inhomogeneity.

Austenitic Iron-Chromium-Nickel Alloy, SRM 479a

The certificate for SRM 479 is in Appendix 9 where the coefficient of variation for 160 points on each of five samples is stated to be not greater than 1.5 percent. The homogeneity characterization is described in detail in reference [10]. The five specimens came from the extreme ends and the 1/4, 1/2, and 3/4 positions of the alloy rod. On each specimen six manual traces were made of the three elements. Two traces were along diameters normal to one another and the remaining four were chords of the specimen. Points were 200 μm apart.

SRM 479 was no longer available when this homogeneity work was being done but testing on the proposed renewal, 479a, was requested. Three traces were prepared for each of the five specimens (samples taken as described previously for SRM 479) using a 1 μm beam and 5 μm steps. Two traces normal to one another and at the center of the specimen covered a distance of about 500 μm . The third trace was used for statistical analyses. In all traces no serious inhomogeneities were observed. The signals for all three elements fell

Glass K-493

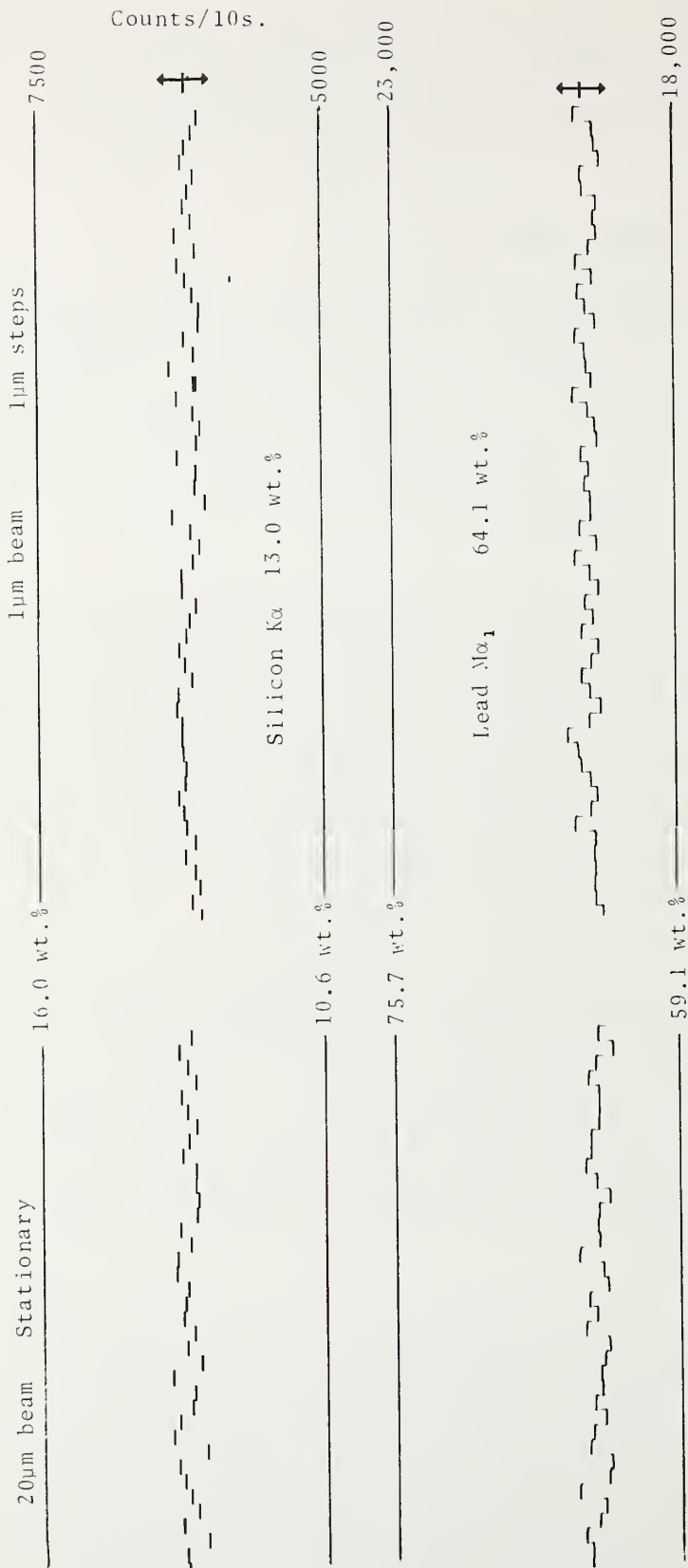


Figure 12. Periodic integrator homogeneity trace of lead and silicon simultaneously recorded from NBS RM Glass K-493 (voltage = 15 kV, beam current = 7.5×10^{-8} A). In the traces on the right, the sample was advanced 1 μm under a 1 μm electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μm electron beam. The double-headed arrows to the right respect a range of $\pm 3\sqrt{N}$ around the average number of counts per 10 seconds, \bar{N} , for the entire trace.

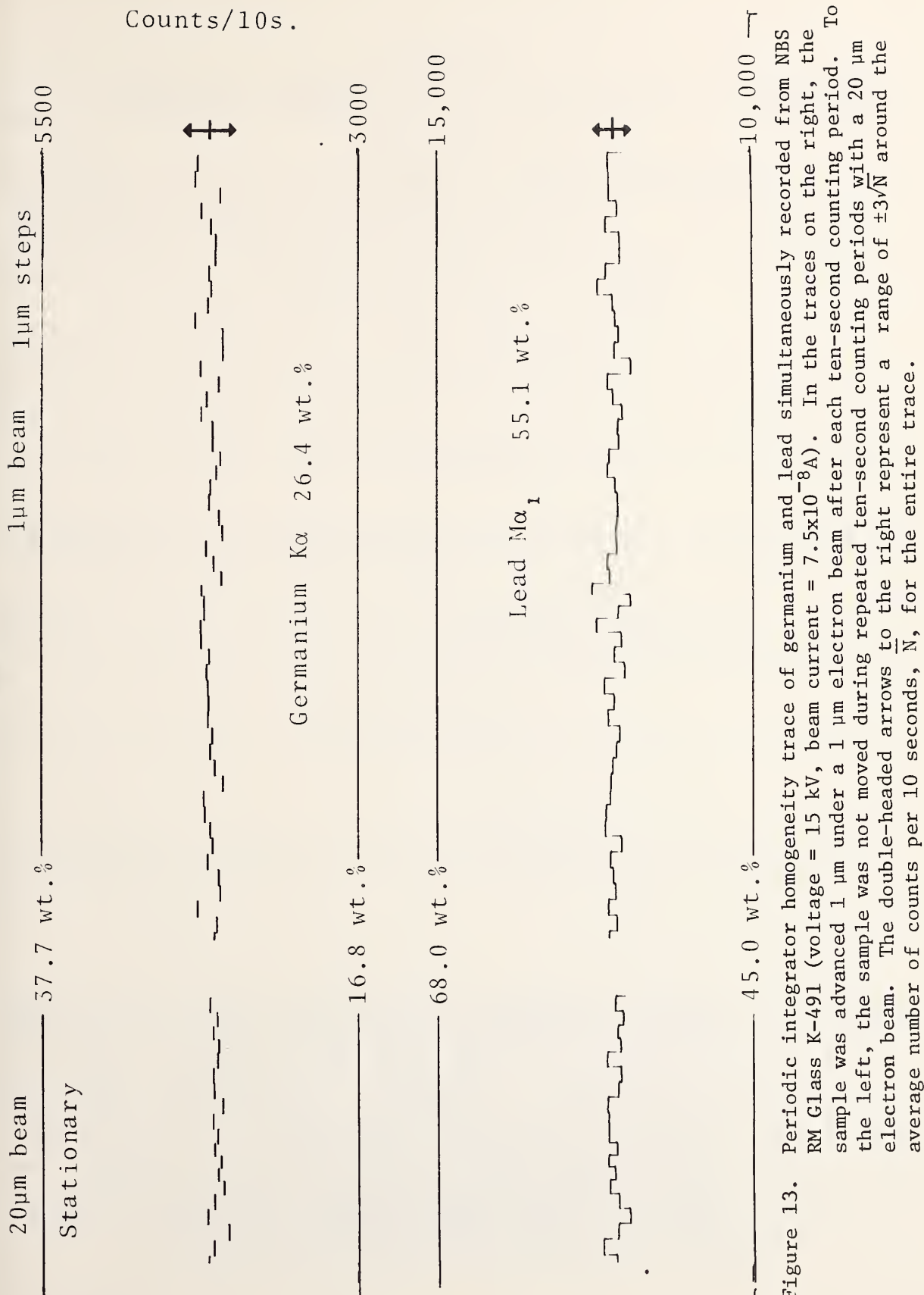


Figure 13. Periodic integrator homogeneity trace of germanium and lead simultaneously recorded from NBS RM Glass K-491 (voltage = 15 kV, beam current = 7.5×10^{-8} A). In the traces on the right, the sample was advanced 1 μm under a 1 μm electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μm electron beam. The double-headed arrows to the right represent a range of $\pm 3\sqrt{N}$ around the average number of counts per 10 seconds, N , for the entire trace.

Glass K-489

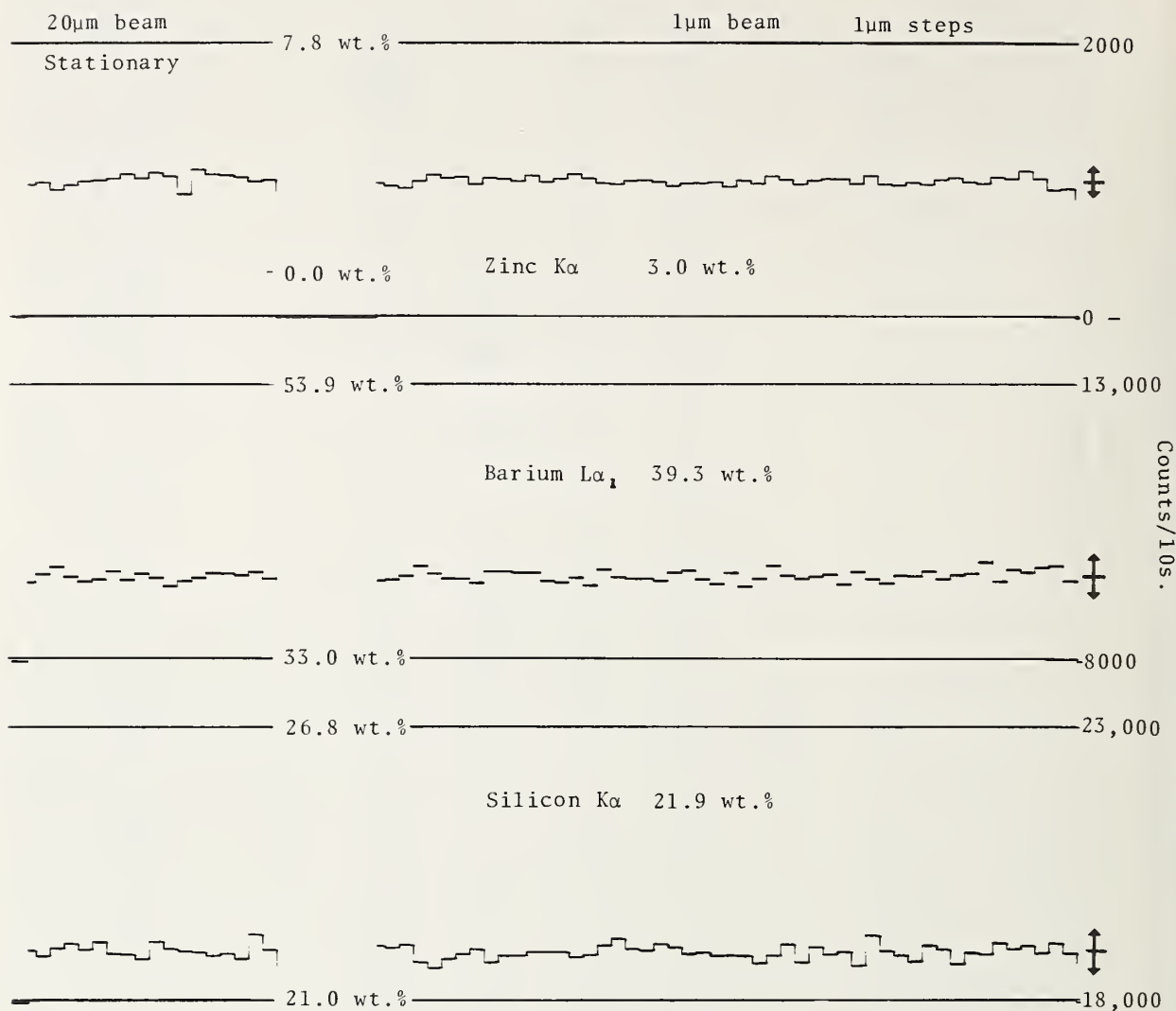


Figure 14. Periodic integrator homogeneity traces of silicon, barium, and zinc simultaneously recorded from NBS RM Glass K-489 (voltage = 15 kV, beam current = 7.5×10^{-8} A). In the trace on the right, the sample was advanced 1 μm under a 1 μm electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μm electron beam. The double-headed arrows to the right represent a range of $\pm 3\sqrt{\bar{N}}$ around the average number of counts per 10 seconds, \bar{N} , for the entire trace.

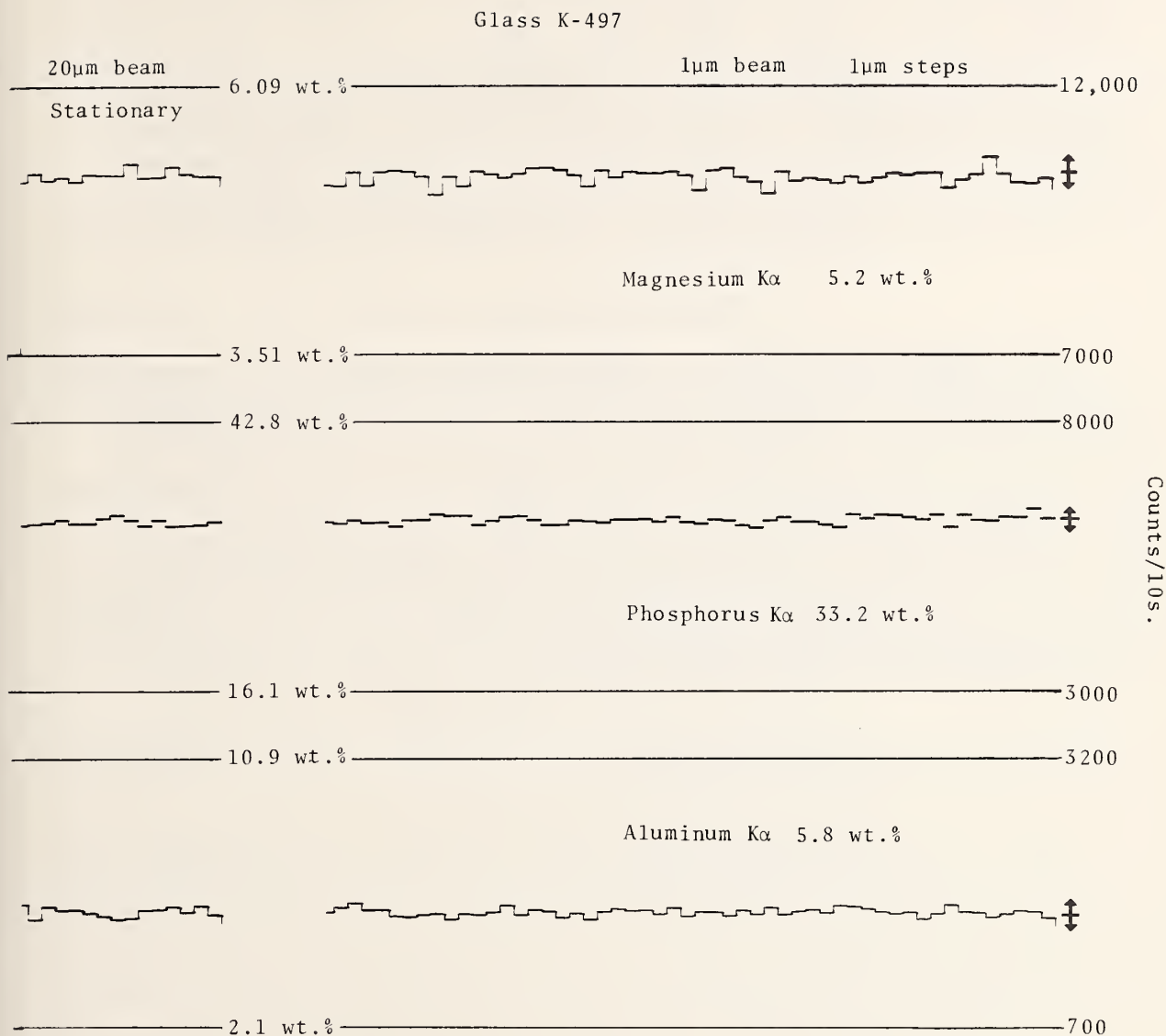


Figure 15. Periodic integrator homogeneity traces of aluminum, phosphorus, and magnesium simultaneously recorded from NBS RM Glass K-497 (voltage = 15 kV, beam current = 7.5×10^{-8} A). In the trace on the right, the sample was advanced 1 μ m under a 1 μ m electron beam after each ten-second counting period. To the left, the sample was not moved during repeated ten-second counting periods with a 20 μ m electron beam. Double-headed arrows to the right represents a range of $\pm 3\sqrt{N}$ around the average number of counts per 10 seconds, \bar{N} , for the entire trace.

within the ± 3 -sigma limits and $\hat{\sigma}_B$, the "between" component of the standard deviation, was in all cases the same or smaller than $\hat{\sigma}_W$, the "within" component.

The five specimens were intercompared by two operators using random sampling. One end sample did appear to be somewhat different from the remaining four. This end will probably be eliminated when the SRM is issued. Complete details of this homogeneity study will appear soon in a new publication on the preparation and analysis of SRM 479a.

We extend our thanks to Dr. J. Mandel and Dr. R. C. Paule for preparing the computer program used in the statistical treatment of the homogeneity scans, to Mrs. M. C. Croarkin and Dr. H. H. Ku for assisting in the statistical handling of the results including the preparation of the equations that appear in Appendix 10, and to Mr. R. L. Myklebust and Ms. B. B. Thorne for adapting the Paule program to our facilities and for preparing the data from the homogeneity scans for the computer. Our thanks also to Mr. J. A. Norris and Mr. R. E. Michaelis for their useful suggestions during the preparation of this manuscript.

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National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1261

AISI 4340 Steel

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.38 ₂	Aluminum (total)	0.02 ₁
Manganese	.66	Niobium	.022
Phosphorus	.015	Tantalum	.020
Sulfur	.017	Boron	.0005
Silicon	.223	Lead	.00002 ₅
Copper	.042	Zirconium	.009
Nickel	1.99	Antimony	.0042
Chromium	0.69 ₀	Bismuth	.0004
Vanadium	.011	Silver	.0004
Molybdenum	.19	Calcium	.00002 ₈
Tungsten	.017	Magnesium	.00018
Cobalt	.030	Selenium	.004
Titanium	.020	Tellurium	.0006
Arsenic	.017	Cerium	.0014
Tin	.010	Lanthanum	.0004
		Neodymium	.0002 ₉

^a This material also is available in the form of chips, SRM 361, for use in chemical methods of analysis; rods, SRM 1095, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 661, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of K. F. J. Heinrich, O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D.C. 20234
January 8, 1976
(Originally issued July 26, 1970
with revisions August 16, 1972, and
attachment February 24, 1975)

J. Paul Cali, Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by J. R. Baldwin, D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the analytical laboratories of Bethlehem Steel Corporation, Sparrows Point Plant, Maryland, R. H. Rouse; Carpenter Technology Corporation, Research and Development Center, Reading, Pennsylvania, E. J. Cramer; The Timken Roller Bearing Company, Steel & Tube Division, Canton, Ohio, R. G. Cover; United States Steel Corporation, Applied Research Laboratory, Monroeville, Pennsylvania, L. Melnick; and Gary Steel Works, Gary, Indiana, E. H. Shipley.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: R. Alvarez, J. R. Baldwin, D. A. Becker, R. K. Bell, R. W. Burke, B. S. Carpenter, E. L. Garner, T. E. Gills, G. J. Lutz, L. A. Machlan, E. J. Maienthal, J. McKay, L. J. Moore, C. W. Mueller, T. J. Murphy, P. J. Paulsen, T. C. Rains, S. D. Rasberry, T. A. Rush, K. M. Sappenfield, B. A. Thompson, S. A. Wicks, and J. Wing.

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements.

Value from a single method of analysis:

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Gold	(<0.00005)	Oxygen	(0.0009)
Zinc	(.0001)	Hydrogen	(<.0005)
Praseodymium	(.00014)	Strontium	^a (<.0005)
Hafnium	(.0002)	Iron (by difference)	(95.6)
Nitrogen	(.0037)		

^aDash indicates "not detected." Value in parenthesis following the dash is the conservative "upper limit" of detection.

Approximate value from heat analysis:

Germanium [0.006]

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1262

AISI 94B17 Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.16 ₀	Aluminum (total)	0.09 ₅
Manganese	1.04	Niobium	.29
Phosphorus	0.042	Tantalum	.20
Sulfur	.038	Boron	.0025
Silicon	.39	Lead	.0004 ₃
Copper	.50	Zirconium	.19
Nickel	.59	Antimony	.012 ₀
Chromium	.30	Silver	.0011
Vanadium	.04 ₁	Calcium	.00014
Molybdenum	.06 ₈	Magnesium	.00062
Tungsten	.20	Tellurium	.0011
Cobalt	.30	Cerium	.0015
Titanium	.084	Lanthanum	.0004
Arsenic	.09 ₂	Neodymium	.0006 ₄
Tin	.016		

^a This material also is available in the form of chips, SRM 362, for use in chemical methods of analysis; rods, SRM 1096, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 662, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of K. F. J. Heinrich, O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D.C. 20234
January 8, 1976
(Originally issued July 27, 1970
with revisions August 16, 1972,
and attachment February 24, 1975)

J. Paul Cali, Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by J. R. Baldwin, D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the analytical laboratories of Allegheny Ludlum Steel Corporation, Research Center, Brackenridge, Pennsylvania, R. B. Friconi; Inland Steel Company, East Chicago, Indiana, R. W. Bley and J. E. Joyce; Republic Steel Corporation, Canton, Ohio, R. W. Jones; and the Youngstown Sheet and Tube Company, Youngstown, Ohio, L. E. Chalker.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: J. R. Baldwin, R. K. Bell, R. W. Burke, D. M. Bouchette, B. S. Carpenter, T. E. Gills, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, J. McKay, L. J. Moore, T. J. Murphy, P. J. Paulsen, T. C. Rains, S. D. Rasberry, B. A. Thompson, J. L. Weber, Jr., and S. A. Wicks.

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements.

Value from a single method of analysis:

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent by weight</u>
Bismuth	(0.002)	Hafnium	(0.0003)
Gold	(<.00005)	Nitrogen	(.00404)
Selenium	(.0012)	Oxygen	(.00107)
Zinc	(.0005)	Hydrogen	(<.0005)
Praseodymium	(.00012)	Strontium	^a -(<.0005)
		Iron (by difference)	(95.3)

^a Dash indicates "not detected." Value in parenthesis following the dash is the conservative "upper limit" of detection.

Approximate value from heat analysis:

Germanium	[0.002]
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National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1263

Cr-V Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.62	Aluminum (total)	0.24
Manganese	1.50	Niobium	.049
Phosphorus	0.02 ₉	Boron	.0009 ₁
Sulfur	.008	Lead	.0022
Silicon	.74	Zirconium	.049
Copper	.09 ₈	Antimony	.002
Nickel	.32	Silver	.0037
Chromium	1.31	Gold	.0005
Vanadium	0.31	Calcium	.00013
Molybdenum	.030	Magnesium	.00049
Tungsten	.046	Tellurium	.0009
Cobalt	.048	Cerium	.0014
Titanium	.050	Lanthanum	.0006
Arsenic	.010	Neodymium	.0006 ₀
Tin	.10 ₄		

^a This material also is available in the form of chips, SRM 363, for use in chemical methods of analysis; rods, SRM 1097, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 663, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of K. F. J. Heinrich, O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D.C. 20234
January 8, 1976
(Originally issued October 2, 1970,
with revisions August 16, 1972,
and attachment February 24, 1975)

J. Paul Cali, Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the analytical laboratories of Climax Molybdenum Company of Michigan, Ann Arbor, Michigan, J. W. Mann and H. E. Trapp; Midvale-Heppenstall Co., Nicetown, Philadelphia, Pennsylvania, W. L. MacBride; Standard Steel Co., Burnham, Pennsylvania, J. Metzger; and The Steel Company of Canada, Hamilton, Ontario, Canada, O. P. Bhargava.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: J. R. Baldwin, R. K. Bell, R. W. Burke, D. M. Bouchette, B. S. Carpenter, T. E. Gills, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, J. McKay, L. J. Moore, T. J. Murphy, P. J. Paulsen, T. C. Rains, S. D. Rasberry, B. A. Thompson, J. L. Weber, Jr., and S. A. Wicks.

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements.

Value from a single method of analysis:

<u>Element</u>	<u>Percent, of weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Tantalum	(0.053)	Hafnium	(0.0005)
Bismuth	(.0008)	Nitrogen	(.0041)
Selenium	(.00016)	Oxygen	(.00066)
Zinc	(.0004)	Hydrogen	(<.0005)
Praseodymium	(.00018)	Strontium	^a (<.0005)
Iron (by difference)	(94.4)		

^a Dash indicates "not certified." Value in parenthesis following the dash is the conservative "upper limit" of detection.

Approximate value from heat analysis:

Germanium	[0.010]
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National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1264

High-Carbon Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

Element	Percent, by weight	Element	Percent, by weight
Carbon	0.87 ₀	Niobium	0.15 ₇
Manganese	.25 ₅	Tantalum	.11
Phosphorus	.01	Boron	.011
Sulfur	.028	Lead	.024
Silicon	.067	Zirconium	.068
Copper	.24 ₉	Antimony	.034
Nickel	.14 ₂	Gold	.0001
Chromium	.06 ₅	Calcium	.00004
Vanadium	.10 ₅	Magnesium	.00015
Molybdenum	.49	Tellurium	.00018
Tungsten	.10 ₂	Cerium	.0002 ₂
Cobalt	.15 ₂	Lanthanum	.00007
Titanium	.24	Neodymium	.00007
Arsenic	.05 ₂		
Tin	.008		

^a This material also is available in the form of chips, SRM 364, for use in chemical methods of analysis; rods, SRM 664, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis; rods, SRM 1098, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis.

CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above. (See **CAUTION** below.)

CAUTION: This standard has been found satisfactory for application in x-ray spectrometric methods of analysis, however, in application testing for optical emission spectrometric analysis some biases were observed - particularly for the carbide-forming elements (Ti, Nb, Zr). This is due to metallurgical structure differences in this particular standard. Reference: Michaelis, R. E., "Homogeneity of SRM's", NBS Spec. Publ. 408, pp 557-571 (U. S. Government Printing Office, 1975). This SRM does not pose a problem for the determination of the elements normally specified in a steel when optical emission methods of analysis are used. However, the user is cautioned that inaccuracies and imprecisions may occur in the determination of the carbide-forming elements, the magnitude of which will depend on the excitation source parameters employed.

Washington, D.C. 20234
January 8, 1976
with revisions August 16, 1972, February 12, 1973,
and attachment February 24, 1975)

J. Paul Cali, Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the analytical laboratories of Ford Motor Co., Dearborn, Michigan, G. A. Nahstoll; Kawecki Beryleo Industries, Inc., Boyertown, Pennsylvania, F. T. Coyle; and Lukens Steel Co., Coatesville, Pennsylvania, J. H. Morris and J. Scott.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: J. R. Baldwin, R. K. Bell, R. W. Burke, D. M. Bouchette, B. S. Carpenter, T. E. Gills, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, J. McKay, L. J. Moore, T. J. Murphy, P. J. Paulsen, T. C. Rains, S. D. Rasberry, B. A. Thompson, J. L. Weber, Jr., and S. A. Wicks.

The overall direction and coordination of the technical measurements at NBS leading to the certification were performed under the direction of K. F. J. Heinrich, O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements.

Value from a single method of analysis:

<u>Element</u>	<u>Percent, by weight</u>	<u>Element</u>	<u>Percent, by weight</u>
Aluminum (total)	(0.0080)	Hafnium	(0.0013)
Bismuth	(.0009)	Nitrogen	(.0032)
Silver	(.00002)	Oxygen	(.0010)
Selenium	(.00021)	Hydrogen	(<.0005)
Praseodymium	(.00003)	Strontium	(.0005)
Iron (by difference)	(96.7)		

Approximate value from heat analysis:

Zinc	[0.001]
Germanium	[.003]

U. S. Department of Commerce
 John T. Connor, Secretary
 National Bureau of Standards
 A. V. Astor, Director

Certificate of Analysis

SPECTROGRAPHIC INGOT IRON AND LOW-ALLOY STEEL STANDARDS

(Revised—May 5, 1965)

NBS No. ¹	461 1161	462 1162	463 1163	464 1164	465 1165	466 1166	467 1167	468 1168
Designation	Low-Alloy Steel A	Low-Alloy Steel B	Low-Alloy Steel C	Low-Alloy Steel D	Ingot Iron E	Ingot Iron F	Low-Alloy Steel G	Low-Alloy Steel H
Element	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
C	0.15	0.40	0.19	0.54	0.037	0.065	0.11	0.26
Mn	.36	.94	1.15	1.32	.032	.11 ₃	.27 ₅	.17
P	.053	.045	0.031	0.017	.008	.012	.033	.023
S	(.02) ²	(.02)	(.02)	(.02)	(.01)	(.01)	(.01)	(.02)
Si	.047	.28	.41	.48	.029	.025	.26	.075
Cu	.34	.20	.47	.094	.019	.033	.067	.26
Ni	1.73	.70	.39	.13 ₅	.026	.051	.088	1.03
Cr	0.13	.74	.26	.078	.004	.011	.036	0.54
V	.024	.058	.10	.29 ₅	.002	.007	.041	.17
Mo	.30	.080	.12	.029	.005	.011	.021	.20
Sn	.022	.066	.013	.043	.001	.005	.10	.009
Ti	(.01)	.037	.010	.004	.20	.057	.26	.011
B	.000 ₂	.000 ₅	.001 ₂	.005	.000 ₁	(.000 ₂)	(.000 ₂)	.009
As	.028	.046	.10	.01 ₉	.010	.014	.14	.008
W	.012	.053	.10 ₅	.022	(.001)	(.006)	.20	.077
Zr	(<.005)	.063	.20	.010	(.002)	(<.005)	.094	(<.005)
Nb	.011	.096	.19 ₅	.057	(.001)	.005	.29	.006
Ta	.002	.056	.15	.069	.001	.002	.23	.005
Al	(.005)	.02 ₃	.02 ₇	.005	.19	.01 ₅	.16	.04 ₂
Co	.26	.41	.01 ₃	.028	.008	.04 ₆	.07 ₄	.16
Pb	(.003)	.006	.012	.020	(<.0005)	(.001 ₃)	.000 ₆	(<.0005)
Ag	(.001 ₅)	(<.0002)	(<.0002)	(.003 ₀)	(.0002 ₅)	(.0004 ₅)	(.004 ₀)	(<.0002)
Ge	(.001 ₅)	(.003 ₀)	(.002 ₅)	(.001 ₅)	(.003 ₅)	(.003 ₀)	(.003 ₀)	(.001 ₀)
O	(.02 ₀)	(.006)	(.007)	(.006)	(.003)	(.005)	(.001)	(.004)
N	(.00 ₆)	(.008)	(.00 ₆)	(.007)	(.005)	(.00 ₆)	(.004)	(.00 ₆)

¹ Sizes: 400 series, rods $\frac{7}{32}$ inch in diameter and 4 inches long.

1100 series, disks $1\frac{1}{4}$ inches in diameter and $\frac{3}{4}$ inch thick.

² Values in parenthesis are *not* certified, but are given for information on the composition.

OVER

Caution: Because these standards contain a graded composition for more than 20 elements, care must be observed in their use to make certain that element lines and internal standard lines are free from interference. All of the analytical points certified have been made to fit a smooth analytical curve at the National Bureau of Standards.

Material for each standard was melted in a one-ton induction furnace at the Naval Research Laboratory and cast into a single ingot. The base material was furnished by Armco Steel Corp. and U. S. Steel Corp. Each ingot was processed by Republic Steel Corp. by forging to a slab having one dimension of the cross section four times that of the other dimension. After cropping top and bottom, the slab was cut lengthwise and the center section corresponding to one-fourth of the original ingot was discarded. The two slab portions were hot rolled to oversize rods and centerless ground to size. About 900 pounds of finished rods were obtained for each standard as follows: 100 pounds of rods 7/32 in. in diameter from the outer sections near the bottom of the original ingot; 400 pounds of rods 1 1/4 in. in diameter from the outer sections near the middle of the original ingot that is currently certified; and 400 additional pounds of rods 1 1/4 in. in diameter which will be issued later as a renewal standard for the 1100 series.

Homogeneity testing was performed by spectrochemical and chemical analyses at the National Bureau of Standards both in slab form and in finished sample form and was found satisfactory for the elements certified.

Chemical analyses and chemical-spectrographic analyses were made on millings cut from the cross section of the 400 and 1100 series rods by the National Bureau of Standards, and on the 1100 series rods by chemical laboratories of the following: American Cast Iron Pipe Co., Armco Steel Corp., Bethlehem Steel Co., Crucible Steel Co. of America, Electro Metallurgical Co., General Motors Corp., Timken Roller Bearing Co., and the U. S. Steel Corp. The values for silver and germanium are the results of spectroscopic determinations only at the National Bureau of Standards. Oxygen and nitrogen values are the result of vacuum fusion determinations at the National Bureau of Standards and at the Research Laboratory of the Jones & Laughlin Steel Corp.

WASHINGTON, D. C. 20234
May 5, 1965.

W. Wayne Meinke, Chief,
Office of Standard Reference Materials.

Certificate of Analysis

Standard Reference Material 481

Gold-Silver Wires for Microprobe Analysis

These standard reference materials are designed for use in quantitative elemental microprobe analysis. Although the selection of this particular system was circumscribed by the requirements of standard reference materials for electron probe microanalysis, the materials will be equally useful for other micro techniques. Accurate chemical characterization and the achievement of homogeneity on a microscopic scale was given special emphasis.

SRM 481 wire	Color code	Nominal comp	Cominco U.S. Bureau American ^a of the Mint ^b			NBS ^c		Average Value ^d	
			Au	Au	Ag	Au	Ag	Au	Ag
			Percent by weight						
A	Gold	Au100	---	---	---	---	---	100.0 ₀	---
B	Gray	Au80-Ag20	80.00	80.02	20.00	80.13	19.93	80.0 ₅	19.9 ₆
C	Yellow	Au60-Ag40	60.01	60.11	39.85	60.04	39.98	60.0 ₅	39.9 ₂
D	Blue	Au40-Ag60	39.99	40.03	59.90	40.06	59.96	40.0 ₃	59.9 ₃
E	Red	Au20-Ag80	22.42	22.42	77.59	22.46	77.56	22.4 ₃	77.5 ₈
F	Silver	Ag100	---	---	---	---	---	---	100.0 ₀

^a The fire assay method was employed for the determination of Au by Cominco American.

^b At the U.S. Bureau of the Mint, Au was determined by fire assay and Ag was determined by titration as AgCl.

^c At NBS, Au was determined from the residue after treatment of the alloys with HNO₃. The Au residue was dissolved in aqua regia, filtered, the Au precipitated by sulfurous acid, and weighed. Ag was determined gravimetrically as AgCl in all four alloys, and also coulometrically in the 80 percent Ag alloy.

^d The results of individual laboratories agree within a range of ± 0.1 percent absolute from the average values. The agreement between results by the different methods and analysts, and the summation of results close to 100 percent for each binary alloy, indicate that the averages are free from significant bias.

The set of standard reference materials, SRM 481, consists of six wires each having a diameter of approximately 0.5 mm and a length of approximately 5 cm. For identification, the four alloy wires were covered with an easily removable colored coating.

The overall direction and coordination of technical measurements leading to certification were performed under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these standards were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

PREPARATION AND PURITY: The standards were prepared by Cominco American Inc. in the form of wires approximately 150 meters long. The end members of the series, as well as the starting materials for the alloys, were of the highest purity grade and precautions were taken to minimize contamination. Two of the alloy standards were heat-treated at NBS to improve microhomogeneity. The pure metal standards were examined by the residual resistivity ratio technique and the total of electrically active impurities in each was estimated to be about 0.001 percent. The gold-silver wires were examined spectrographically for metallic impurities; no significant impurities were found at detection limits ranging from 0.0001 to 0.010 percent.

LONGITUDINAL HOMOGENEITY: Variation in composition along the full length of each alloy wire was investigated by electron probe microanalysis for areas 25 μm diameter on cross sections at three to five positions along the wire including the two ends. The observed differences in composition for the positions, expressed as the range between the highest and lowest values for each alloy, were as follows:

Nominal Composition	Au80	Au60	Au40	Au20
Observed range ^a	0.3%	0.6%	0.3%	0.5%

Homogeneity along the wires was also tested by measurement of the residual resistivity ratio. These measurements indicated that the variation (macroscopic) of composition along all standard wires was less than 0.1 percent absolute. Further information on longitudinal homogeneity of the wires was obtained by determinations of Au at the extreme ends of the alloy wires by the Bureau of the Mint; the data also indicate that the extreme variation along the wires is less than 0.1 percent absolute.

TRANSVERSE AND MICRO HOMOGENEITY: Variation in composition within the above mentioned cross sections of the wires was investigated by electron probe microanalysis. For each cross section, measurements were made along two diagonals at right angles. On each diagonal, determinations were made at 25 points, 1 μm or less in diameter, starting and ending at approximately 25 μm from the edge. For each alloy, the element which could be determined with the better precision was used in the evaluation. The variation was calculated in terms of the standard deviation for an individual determination for each traverse. In the table below, the variation is presented as the range between the lowest and highest observed standard deviations for the six to eight traverses performed on each alloy.

Nominal Composition	Element Determined	Range of Standard Deviation for Traverses ^a
Au80	Ag	0.08 – 0.11%
Au60	Au	.08 – .16
Au40	Au	.08 – .13
Au20	Au	.12 – .37

The homogeneity on a microscopic scale was further investigated by performing quantitative measurements in two arrays of 10×10 points ($1 \mu\text{m}$ diameter) on each of the cross sections. The distance between adjacent points was $3.5 \mu\text{m}$. This was repeated on several cross sections so that 6 to 8 arrays were obtained on each alloy. For the element which could be measured with better precision, the range is given between the lowest and highest observed standard deviation for an individual determination for the 6 to 8 arrays for each alloy.

Nominal Composition	Element Evaluated	Range of Standard Deviations for Arrays ^a
Au80	Ag	0.09 – 0.15 %
Au60	Au	.18 – .57
Au40	Au	.19 – .25
Au20	Au	.11 – .66

(Note: This range and the two ranges in the following tables are close to the precision of the method and should be considered upper limits of estimates of inhomogeneity.)

Extensive homogeneity studies were performed with the electron probe microanalyzer at NBS by M. A. Giles, R. L. Myklebust, C. E. Fiori, and K. F. J. Heinrich. Measurements of residual resistivity ratio were made at NBS, Boulder, Colorado, by R. L. Rutter, J. G. Hust, and R. L. Powell. Heat treatment of the alloys at NBS was performed by G. E. Hicho and M. R. Meyerson. Spectrographic survey analyses were made at NBS by V. C. Stewart. Determinations of composition were made at Cominco American, Inc., Spokane, Washington, by T. A. Rice; at the U.S. Bureau of the Mint, Washington, D. C., by H. G. Hanson, Jr.; and at NBS by R. A. Durst, G. Marinenko, and C. E. Champion.

Certificate of Analysis

STANDARD REFERENCE MATERIAL 482 Gold-Copper Wires for Microprobe Analysis

These standard reference materials are designed for use in quantitative elemental microprobe analysis. Although the selection of this particular system was circumscribed by the requirements of standard reference materials for electron probe microanalysis, the materials will be equally useful for other micro techniques. Accurate chemical characterization and the achievement of homogeneity on a microscopic scale were given special emphasis.

SRM 482 wire	Color code	Nominal composition	Cominco American ^a Au	U.S. Bureau of the Mint ^b		NBS ^c		Average value ^d	
				Au	Cu	Au	Cu	Au	Cu
				Percent by weight					
A	Gold	Au100	—	—	—	—	—	100.0 ₀	—
B	Gray	Au80 — Cu20	80.10	80.13	19.81	80.21	19.85	80.1 ₅	19.8 ₃
C	Blue	Au60 — Cu40	60.30	60.37	39.66	60.41	39.62	60.3 ₆	39.6 ₄
D	Yellow	Au40 — Cu60	40.12	40.06	59.88	40.11	59.97	40.1 ₀	59.9 ₂
E	Red	Au20 — Cu80	20.04	20.12	79.84	20.21	79.86	20.1 ₂	79.8 ₅
F	Copper	Cu100	—	—	—	—	—	—	100.0 ₀

^aThe fire assay method was employed for the determination of Au by Cominco American.

^bAt the U. S. Bureau of the Mint, Au was determined by fire assay and Cu was determined by electrodeposition.

^cAt NBS, Au was determined by precipitation from solution; Cu was determined by electrodeposition.

^dThe results of individual laboratories agree within a range of $\pm 0.1\%$ absolute from the average values. The agreement between results by the different methods and analysts, and the summation of results close to 100% for each binary alloy, indicate that the averages are free from significant bias.

The set of standard reference materials, SRM 482, consists of six wires each having a diameter of approximately 0.5 mm and a length of approximately 5 cm. For identification, the four alloy wires were covered with an easily removable colored coating.

The overall direction and coordination of technical measurements leading to certification were performed under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these standards were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

PREPARATION AND PURITY: The standards were prepared by Cominco American, Inc. in the form of wires approximately 150 meters long. The end members of the series, as well as the starting materials for the alloys, were of the highest purity grade and precautions were taken to minimize contamination. Two of the alloy standards were heat-treated at NBS to improve microhomogeneity. The pure metal standards were examined by the residual resistivity ratio technique and the total of electrically active impurities in each was estimated to be about 0.001%. The gold-copper wires were examined spectrographically for metallic impurities; no significant impurities were found at detection limits ranging from 0.0001 to 0.010%.

LONGITUDINAL HOMOGENEITY: Variation in composition along the full length of each alloy wire was investigated by electron probe microanalysis for areas 25 μm diameter on cross sections at three positions along the wire including the two ends. The observed differences in composition for the positions, expressed as the range between the highest and lowest values for each alloy, were as follows:

Nominal Composition	Au80	Au60	Au40	Au20
Observed range*	0.3%	0.7%	0.9%	0.9%

Homogeneity along the wires was also tested by measurement of the residual resistivity ratio. These measurements indicated that the variation (macroscopic) of composition along all standard wires was less than 0.1% absolute. Further information on longitudinal homogeneity of the wires was obtained by determinations of Au at the extreme ends of the alloy wires by the Bureau of the Mint; the data also indicate that the extreme variation along the wires is less than 0.1% absolute.

TRANSVERSE AND MICRO HOMOGENEITY: Variation in composition within the above mentioned cross sections of the wires was investigated by electron probe microanalysis. For each cross section, measurements were made along two diagonals at right angles. On each diagonal, determinations were made at 25 points, 1 μm or less in diameter, starting and ending at approximately 25 μm from the edge. For each alloy, the element which could be determined with the better precision was used in the evaluation. The variation was calculated in terms of the standard deviation for an individual determination for each traverse. In the table below, the variation is presented as the range between the lowest and highest observed standard deviations for the six traverses performed on each alloy.

Nominal Composition	Element Determined	Range of Standard Deviations for Traverses*
Au80	Cu	0.09 – 0.24%
Au60	Cu	.16 – .27
Au40	Au	.13 – .23
Au20	Au	.13 – .20

The homogeneity on a microscopic scale was further investigated by performing quantitative measurements in two arrays of 10×10 points ($1 \mu\text{m}$ diameter) on each of the cross sections. The distance between adjacent points was $3.5 \mu\text{m}$. This was repeated on several cross sections so that 6 arrays were obtained on each alloy. For the element which could be measured with better precision, the range is given between the lowest and highest observed standard deviation for an individual determination for the 6 arrays for each alloy.

<u>Nominal Composition</u>	<u>Element Determined</u>	<u>Range of Standard Deviations for Arrays*</u>
Au80	Cu	0.19 – 0.28%
Au60	Cu	.28 – .37
Au40	Au	.25 – .31
Au20	Au	.12 – .20

*The ranges indicated are close to the precision of the method and should be considered upper limits of estimates of inhomogeneity.

Extensive homogeneity studies were performed with the electron probe microanalyzer at NBS by M. A. Giles, D L. Vieth, R. L. Myklebust, C. E. Fiori, and K. F. J. Heinrich. Measurements of residual resistivity ratio were made at NBS, Boulder, Colorado, by R. L. Rutter and R. L. Powell. Heat treatment of the alloys at NBS was performed by G. E. Hicho and M. R. Meyerson. Spectrographic survey analyses were made at NBS by V. C. Stewart. Determinations of composition were made at Cominco American, Inc., Spokane, Washington, by T. A. Rice; at the U. S. Bureau of the Mint, Washington, D. C., by H. G. Hanson, Jr.; and at NBS by J. R. Baldwin and R. A. Durst.



C. R. Smith
Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material 480

Tungsten—20% Molybdenum Alloy

Electron Microprobe Standard

SRM No.	Tungsten weight percent	Molybdenum weight percent
480	78.5	21.5

This standard is a composite consisting of a core of W—20 wt % Mo alloy wire (1 mm diameter), embedded in pure Mo rod (5 mm diameter) onto which has been electroplated a layer of pure W (1 mm thick). Each standard is 1 mm thick.

Chemical analyses were performed by the Analytical Chemistry Division, NBS. Two independent methods were employed the first of which utilized an ion exchange separation, followed by gravimetric determination of the ignited oxides. An average value of 78.5 wt % was obtained for W with a standard deviation for a single determination of ± 0.3 wt % ($n = 4$). For Mo the average value obtained was 21.5 wt % with a standard deviation of ± 0.2 wt % ($n = 4$). Analyst — R. K. Bell. A spectrophotometric thiocyanate method was used for the determination of Mo only. In this method, Mo was reduced with Sn^{2+} and the color system stabilized with butyl cellosolve. An average value of 21.7 wt % was obtained with a standard deviation for the single determination of ± 0.2 wt % ($n = 6$). Analyst — E. R. Deardorff.

Homogeneity testing by means of the NBS electron microprobe was performed on four selected samples of the composite rod using an operating voltage of 20 kV, a monitor current (proportional to beam current) of 2 microamperes corresponding to a specimen current of 0.22 microamperes. The $L\alpha$ lines of the W and Mo were monitored by means of LiF(W) and EDDT(Mo) monochromator — proportional counter channels. The dead time in each channel was 2.3 microseconds. The x-ray emergence angle was 52.5° . A quantitative raster scanning procedure was employed to obtain the homogeneity data which is summarized in the following table for three of the four samples. Analyst — H. Yakowitz.

Homogeneity Characterization Results

Specimen	Condition	CV — Mo ^a	CV — W ^a	Determinations (each element)
EMS-72	Lightly etched	2.47	1.24	400
EMS-73	Unetched	2.37	1.55	400
EMS-74	Lightly etched	2.54	1.34	500

$$^a \text{CV} = \frac{(100) (\text{Std. Dev.})}{\text{Mean number of counts}}$$

Approximate mean number of counts accumulated for W = 500,000

Approximate mean number of counts accumulated for Mo = 45,000

The material for the standard was prepared in the Lamp Metals and Components Department, General Electric Company, Cleveland, Ohio, through the use of a powder metallurgy process involving high-purity metal powders.

Details of the preparation, testing, and intended use of this standard can be found in NBS Spec. Publ. 260-16, Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: W—20% Mo Alloy Prepared by Powder Metallurgical Methods, H. Yakowitz, R. E. Michaelis, and D. V. Vieth, (in press).

The overall direction and coordination of technical measurements leading to the certification were performed under the chairmanship of J. R. DeVoe.

The technical and support aspects involved in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 478

Microprobe Standard - Cartridge Brass

This Standard Reference Material consists of one specimen each of chill cast material (SRM C1102) and wrought material (SRM 1102). The cast material is supplied as a cube 6 mm on an edge; the chill cast face is polished. The wrought material is supplied as a right circular cylinder 6 mm diameter by 6 mm high. Some sixteen elements are certified for their chemical composition in SRM's C1102 and 1102. However, at the micrometer level of spatial resolution these brasses comprising SRM 478, are certified to be homogeneous with respect to copper and zinc only.

CERTIFIED CHEMICAL CHARACTERIZATION

<u>SRM</u>	<u>COPPER</u>	<u>ZINC</u>
478 (both specimens)	72.8 ₅	27.1 ₀

The material for each component of the standard was melted and cast at the Naval Research Laboratory, Washington, D. C. High-purity metals were used either directly or in the preparation of master alloys. Approximately 325-kg heats were melted under a charcoal cover in a high-frequency induction furnace and the molten metal cast on a massive water-cooled plate to provide rapid unidirectional solidification. The casting for each standard was about 68.5 cm (27 in) in diameter and 8.9 cm (3 1/2 in) thick.

The material for the chill-cast samples was obtained from the area of the casting nearest the chill-cast face. Samples were originally finished to a size 31 mm (1 1/4 in) square, 19 mm (3/4 in) thick.

The material for the wrought samples was obtained after removal of the chill-cast material and discard of about 19 mm (3/4 in) thickness from the slab top. Strips of this material were forged, fully annealed, and finished to samples 31 mm (1 1/4 in) in diameter, 19 mm (3/4 in) thick.

The microprobe specimens were cut by electrical-discharge machining into the form provided as SRM 478. The chill-cast face was metallographically polished by mechanical means prior to the electrical-discharge machining.

Samples for chemical analysis were prepared in the form of millings taken from the cross section of the finished samples of both the chill-cast and wrought material.

Washington, D. C. 20234

February 28, 1974

J. Paul Cali, Chief

Office of Standard Reference Materials
(over) 63

Chemical analyses were performed in the NBS Analytical Chemistry Division by R. Alvarez, R. K. Bell, R. W. Burke, A. P. Landgrebe, E. E. Maczkowske, E. J. Maienthal, G. W. Smith, and R. K. Wolford. (See NBS Miscellaneous Publ. 260-7 99PP (1965) for details.)

Cooperative analyses for certification were performed in the analytical laboratories of Anaconda American Brass Co., Waterbury, Conn., O. P. Case and K. M. O'Brien; Department of Mines and Technical Surveys, Mines Branch, Ottawa, Ontario, Canada, A. E. LaRoche, E. M. Penner, C. H. McMaster, and W. R. Inman; Mueller Brass Co., Port Huron, Mich., S. C. Richards, R. Stevens, and A. Stuever.

Technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CERTIFIED HOMOGENEITY CHARACTERIZATION

The homogeneity of Cu and Zn in SRM 478 was investigated by means of the electron probe microanalyzer. Two separate channels with LiF analyzing crystals and sealed proportional detectors were employed. The instrument was operated at 30 keV with probe currents of 100 na. The probe diameter was approximately one micrometer. The count rate for Cu was on the order of 13,500 c/s, whereas the count rate for Zn was on the order of 4,000 c/s. Signal-to-background ratios for Zn were greater than 100 to 1. Results of homogeneity testing follow:

Element	Coefficient of variation for counting	Standard deviation (%) computed from experiment	Analytical range (two standard deviation limits of composition at the three micrometer level of spatial resolution)
Zn ^a	0.0036	0.79	26.7 to 27.5
Cu ^a	.0027	.72	71.8 to 73.8
Zn ^b	.0036	2.2	25.9 to 28.3
Cu ^b	.0019	1.0	71.1 to 74.6

^aCast

^bWrought

SRM-478 contains inclusions that are extremely small and appear to be essentially round indicating that they are spheres in three dimensions. The size of the inclusions ranges from sub-micrometer to about two micrometers in diameter. They are dull grey in color. In the cast form, they are randomly distributed while in the wrought form they are usually found at grain boundaries. There are about 800 inclusions per cubic millimeter of brass.

Wavelength scans were taken of many inclusions in both forms of the brass to identify the elements present. The presence of reasonably large amounts of Pb and S was noted. Some variable amounts of Zn, Si, and Al were found. Except for Zn, these elements are not expected to be uniformly distributed within the brass; the concentration of these elements varied considerably from inclusion to inclusion.

Details of the homogeneity testing are contained in NBS Misc. Publ. 260-10, 28PP (1965).

Electron probe microanalysis of SRM 478 was performed at NBS and at seven other laboratories. [See ASTM Spec. Tech. Publ. 430, 343 (1968) for details.] The results confirm the homogeneity levels and analysis limits stated above. SRM 478 should be especially useful for establishing correct relative intensity ratios between specimen and standard.

Caution should be observed in the use of the chill-cast samples. Determinations made on other than the chill-cast, or test surface, are not recommended because of the unidirectional solidification.

Certificate of Analysis

Standard Reference Material 483

Fe-3Si Alloy Microprobe Standard^a

This standard is characterized for chemical homogeneity of iron and silicon at the micrometer level of spatial resolution and is satisfactory for use as a homogeneous material for electron probe microanalysis.

SRM	Silicon	Iron (by difference)
	Weight, percent	
483	3.22 ^b ± 0.02 ^c	96.7 – 96.8

^aSize: 3 mm × 3 mm × 0.28 mm thick. The material is from coarse-grained sheet stock having the so-called Goss orientation in which a [110] grain is parallel to the surface and [001] is the rolling direction. Each sample is supplied HF etched and ready for metallographic mounting and polishing.

^bDetermination of silicon involved 49 samples of SRM 483. SRM 125b, certified at 2.89 wt. % Si, was used as a control standard and 2.90 wt. % Si was found.

Method: One gram samples were dissolved in hydrochloric and nitric acids. A double dehydration of the silicon with perchloric acid was made with an intervening filtration. The weight of silicon present was determined from the loss resulting from treatment with hydrofluoric acid. Analyst – R. A. Paulson, NBS Analytical Chemistry Division.

^cStandard deviation of a single determination based on results obtained on SRM's 483 and 125b, but also including similar method error estimations from previous determinations.

HOMOGENEITY TESTING AND QUANTITATIVE ANALYSIS BY ELECTRON PROBE MICROANALYSIS

Homogeneity was checked by means of quantitative raster scanning in which a square matrix (1.1 mm × 1.1 mm) of individual points is analyzed by the microprobe. Each matrix represents 400 separate analyses. Six selected matrices were run for iron and silicon with three of these rerun. The coefficient of variation for both the iron and silicon is less than one percent. Analysts – H. Yakowitz, NBS Metallurgy Division, and C. E. Fiori, NBS Analytical Chemistry Division.

Quantitative microprobe analysis of this alloy gave a silicon content of 3.14 wt. % and an iron content of 96.9%. Analyst – H. Yakowitz, NBS Metallurgy Division.

Details of the microprobe testing and analyses, as well as the sample preparation, are given in NBS Special Publication 260-22, Standard Reference Materials: Homogeneity Characterization of Fe-3Si Alloy, H. Yakowitz, C. E. Fiori, and R. E. Michaelis, Feb. 1971.

The technical and support aspects involved in the preparation, certification, and issuance of this standard were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

National Bureau of Standards

Report of Investigation

Glasses for Microanalysis RM 30

Glass Fibers for Microanalysis RM 31

K. F. J. Heinrich, D. H. Blackburn, M. M. Darr, C. E. Fiori,
R. B. Marinenko, D. E. Newbury, and J. A. Small

Five types of glasses are available as research materials (RM) in the form of bulk samples, 2x2x20 mm, and as fibers ranging from 10-100 μ m in diameter and 50-60 mm long.

The major constituents of the glasses were selected so that a variety of matrices of differing average atomic numbers would be represented. For each of the five matrices, there are two glasses - one with and one without the low-concentration additives.

Applications

These Reference Materials were developed for use in microanalysis techniques such as electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS). These homogeneous vitreous solids containing known low-concentration additions of several elements should be useful in the analysis of complicated unknowns. The fibers were drawn for use in particulate analyses for which there presently are no well-characterized standards of complex composition and simple shape.

Preparation of the Glasses

The compounds employed in the manufacture of the glasses were reagent-grade materials or compounds of equal or greater purity. Usually the oxides were used, but where this was not possible, the carbonates, nitrates, or phosphates were used. After weighing, the batch materials were mixed thoroughly as dry powders prior to melting.

The glass components were melted in 300 ml platinum crucibles in electrically heated furnaces in an oxidizing atmosphere (air). To ensure homogeneity, the glasses were stirred from four to six hours with a motor-driven, double-bladed, propeller-type stirrer made of a platinum-rhodium-alloy. Melting and stirring temperatures ranged from 900-1400 °C depending upon the glass being prepared. After completion of the melting and stirring operations, the glass was cast into a rectangular block and annealed to remove residual strain.

Composition

The compositions in weight percent of the oxides in the glasses are listed in the attached table. These are nominal values calculated from the weight of the component added to the melt during the manufacture of the glass. Preliminary analyses with the electron probe indicate that these nominal values are accurate to five percent relative or better for the major constituents, and to 20 percent relative for the low-concentration additions.

A thorough analysis and homogeneity study of these glasses by the electron probe is now in progress. Other analytical methods are also being used when necessary. This report will be revised when the analytical results are available.

Preparation of Bulk Samples

The bulk samples, approximately 2x2x20 mm, were cut from the large annealed rectangular glass block. A precision wafering saw was used with a 0.071x15.2 cm, (0.028 x 6") 100 grit diamond wheel and a petroleum-based coolant. An acetone-soluble adhesive was used to mount the glass block and slices onto the cutting plate. Several 2 mm slices were cut from near the middle of the glass block. These slices were in turn cut at 2 mm intervals. The glass slices were removed from the cutting plate and rinsed with acetone several times to remove all traces of adhesive.

Preparation of Fibers

Preliminary to drawing fibers, a glass fragment was melted in a platinum boat that was heated directly by an electric current. The fiber was formed by drawing a thread of molten glass through an orifice in the bottom of the platinum boat. The continuous glass fiber was wound onto a 25.4 cm (10 inch) diameter metal drum driven by a variable speed electric motor (1000-4000 rpm). Different orifice sizes and drum speeds were used in drawing the fibers, depending upon the viscosity and surface tension of each glass. This procedure requires a minimum amount of working time and low temperatures, therefore minimizing compositional changes due to vaporization.

1. Fiori, C. E.; Heinrich, K. F. J.; Marinenko, R. B.; Darr, M. M.; Blackburn, D. H.; Newbury, D. E.; and Small, J. A., "An Overview of the Glass Standards Program for Microanalysis at the National Bureau of Standards," paper to be presented at the Joint Meeting of Electron Microscopy Society of America and Microbeam Analysis Society, Miami Beach, Fla., August 1976.
2. Marinenko, R. B.; Heinrich, K. F. J.; Fiori, C. E.; Darr, M. M.; Blackburn, D. H.; Newbury, D. E.; and Small, J. A., "Glass Standards for Microanalysis of Particles," paper to be presented at Federation of the Analytical Chemistry and Spectroscopy Societies 3rd Annual Meeting, Philadelphia, Pa., November, 1976.

Glasses for Microanalysis

<u>Melt No.</u>	<u>K-456</u>	<u>K-493</u>	<u>K-453</u>	<u>K-491</u>	<u>K-458</u>	<u>K-489</u>	<u>K-495</u>	<u>K-490</u>	<u>K-496</u>	<u>K-497</u>
Composition in Weight Percent										
SiO ₂	28.77	27.89	---	0.19	49.38	46.76	---	0.42	---	0.27
PbO	71.23	69.08	58.72	59.35	---	1.28	---	1.55	---	.99
GeO ₂	---	---	41.28	37.98	---	---	---	---	---	---
BaO	---	---	---	---	46.80	43.88	---	---	---	---
ZnO	---	---	---	---	3.82	3.72	---	---	---	---
P ₂ O ₅	---	---	---	---	---	---	---	---	79.54	76.03
MgO	---	---	---	---	---	---	---	---	9.03	8.64
Al ₂ O ₃	---	0.20	---	0.16	---	0.29	20.00	18.68	11.43	10.92
B ₂ O ₃	---	.14	---	.11	---	.20	75.00	70.00	---	0.15
ZrO ₂	---	.49	---	.40	---	.70	---	0.85	---	.54
TiO ₂	---	.32	---	.26	---	.46	---	.55	---	.35
CeO ₂	---	.68	---	.56	---	.98	---	1.19	---	.76
Ta ₂ O ₅	---	.88	---	.72	---	1.26	---	1.53	---	.98
Fe ₂ O ₃	---	.32	---	.26	---	0.46	---	0.55	---	.35
Li ₂ O	---	.001	---	.001	---	.002	5.00	4.67	---	.001

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 479

Fe-Cr-Ni Alloy Microprobe Standard

This Standard Reference Material is characterized for chemical homogeneity of iron, chromium, and nickel at the micrometer level of spatial resolution and is satisfactory for use as a homogeneous material for electron probe microanalysis. It is issued in wafer form, 4.6 mm in diameter and 1 mm thick, in the as-cut condition after electrical discharge machining.

CERTIFIED CHEMICAL CHARACTERIZATION

SRM	Nickel ^a	Chromium ^a Weight, percent	Iron (by difference) ^b
479	10.7	18.3	71.0

^a Nickel was determined gravimetrically by the nickel dimethylglyoxime method; chromium was oxidized to chromate and titrated with a standard ferrous ammonium sulfate solution. Analyst - R. A. Paulson

^b Pure chromium, nickel, and iron were used in the preparation of this alloy (99.9% minimum purity for each element). (For information only, carbon was determined to be 0.012%.)

CERTIFIED HOMOGENEITY CHARACTERIZATION

Homogeneity testing for iron, chromium, and nickel was carried out by means of the NBS electron microprobe with an operating voltage of 20kV and spectrometers equipped with LiF crystals and sealed proportional detectors. Approximately 160 analyses were made on each of five samples taken from the original alloy rod ends, and the 1/4, 1/2, and 3/4 positions, respectively. The observed coefficient of variation was not greater than 1.5% for any of the three elements. For sixteen determinations made for each element, the observed 99% confidence intervals about the means were (Wt.%):

Iron	± 0.80
Chromium	± 0.20
Nickel	± 0.12

Analyst - H. Yakowitz

The preparation of the original alloy ingot and subsequent thermal and mechanical processing steps to improve chemical homogeneity were conducted by D. P. Fickle and A. W. Ruff.

The technical and support requirements associated with the issuance of the Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Technical details concerning the preparation and characterization of this SRM are given in NBS Special Publication 260-43, Preparation and Homogeneity Characterization of an Austenitic Iron-Chromium-Nickel Alloy.

Washington, D.C. 20234
October 16, 1972

J. Paul Cali, Chief
Office of Standard Reference Materials

SUPPLEMENTARY INFORMATION

The original alloy ingot was produced by the arc fusion method in an inert gas atmosphere of argon, gettered by titanium. The ingot was repeatedly swaged, and annealed in a sealed quartz tube until the final diameter of 4.6 mm was reached. A diffusion annealing step was included for 5 days at 1120 °C.

The rod was cut into wafers approximately 1 mm thick by electro-discharge machining in an organic solvent. The specimens selected for homogeneity characterization were ground on a series of SiC papers, followed by 6 μ m diamond and then 1/4 μ m diamond particle polishing. Final polishing was done using 0.05 μ m Al₂O₃ particles on Gamal cloth.

Electron probe microanalysis was performed on the 1/4, 1/2, 3/4 specimens using pure element standards (M. M. Darr, H. Yakowitz, C. E. Fiori, and R. L. Myklebust). Results are as follows:

<u>Element</u>	<u>Voltage (kV)</u>	<u>Concentration (Wt. %)</u>
Fe	15	70.8
Fe	20	70.1
Fe	25	71.7
Fe	30	71.1
Cr	15	18.4
Cr	20	19.2
Cr	25	19.2
Cr	30	19.3
Ni	15	10.9
Ni	20	10.7
Ni	25	10.7
Ni	30	10.7

Prior to the production of SRM 479, a portion of the original ingot was used to produce foil specimens for subsequent determination of the stacking fault energy of the alloy over the temperature range 25 to 325 °C using transmission electron microscope methods (R. M. Latanision and A. W. Ruff, *Met. Trans.* 2, 505 (1971)). Those results indicated that satisfactory solute homogeneity should be obtained by a suitable thermal and mechanical processing program.

Appendix 10

The equations used in the computer program for the determination of standard inhomogeneity are as follows. A mean intensity, $y_{i.}$, is calculated from each group of replicate measurements on a single point. This is,

$$y_{i.} = \frac{1}{s} \sum_{j=1}^s y_{ij} \quad (2)$$

where

y_{ij} = the number of counts observed at the i^{th} step
and the j^{th} replicate reading on this point.

s = the total number of readings on the same point.
For the entire homogeneity scan a "grand" mean intensity, $y_{..}$, is calculated according to

$$y_{..} = \frac{1}{r} \sum_{i=1}^r y_{i.} \quad (3)$$

where,

r = the total number of points sampled.

The estimates of the components of variance of y_{ij} are then calculated according to the equations below. The total variance is

$$\hat{\sigma}_T^2 = \frac{\sum (y_{i.} - y_{..})^2}{r-1} \quad (4)$$

The "within" component is

$$\hat{\sigma}_W^2 = \frac{\sum (y_{ij} - y_{i.})^2}{r(s-1)} \quad (5)$$

And the "between" component is

$$\hat{\sigma}_B^2 = \hat{\sigma}_T^2 - \frac{\hat{\sigma}_W^2}{s} \quad (6)$$

These components of variance are calculated from the total number of counts, including the background. But the expression of uncertainty in terms of concentration is more useful. The background intensity is subtracted from the line intensity in concentration calculations. The variance for the number of net counts above the background is estimated by

$$\hat{\text{Var}} (\bar{X} - \bar{B}) = \frac{\hat{\sigma}_W^2 + s\hat{\sigma}_B^2}{rs} + \frac{\bar{B}}{L} \quad (7)$$

where,

$$\bar{X} = y_{..}$$

\bar{B} = average of the background counts,

and,

L = the number of times the background is read. The uncertainty in the number of counts at the 99.7 percent confidence level, assuming no systematic error, is $\pm U_2$,

$$U_2 = 3 \left[\frac{\hat{\sigma}_W^2 + s\hat{\sigma}_B^2}{rs} + \frac{\bar{B}}{L} \right]^{\frac{1}{2}} \quad (8)$$

Assuming a linear relationship between the number of counts above the background and the concentration, where

$$\frac{\% \text{conc.}}{(\bar{X} - \bar{B})} = c \quad (9)$$

the uncertainty, $\pm U_1$, in terms of concentration and including the uncertainty in the chemical analysis is given by

$$U = \left\{ 9c^2 \left[\frac{\hat{\sigma}_W^2 + s\hat{\sigma}_B^2}{rs} + \frac{\bar{B}}{L} \right] + U_1^2 \right\}^{\frac{1}{2}} \quad (10)$$

where,

U_1 = the uncertainty in the concentration given in the certificate.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) A simple routine technique for studying homogeneity in the micrometer range with the electron microprobe has been developed. For graphic display, a digital periodic integrator is used. In conjunction with scalers and a stepping motor on the sample stage, traces similar to industrial control charts based on a comparison of the experiment with the expected (Poisson) counting statistics are quickly obtained. A computer program has been developed to numerically evaluate sample homogeneity. Several Standard Reference Materials (SRMs) have been tested. These include the iron and steels (SRMs 661-664, 461, and 463), the gold-copper and gold-silver alloys (SRMs 481 and 482), the tungsten-20 percent molybdenum alloy (SRM 480), cartridge brass (SRM 478), the iron-chromium-nickel alloy (SRM 479a). A Research Material, Glasses for Microanalysis (RM-30), has also been tested.			
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